Supporting Information

Nickel-Catalyzed Carbonylative Domino Cyclization of Arylboronic Acid Pinacol Esters with 2-Alkynyl Nitroarenes Toward *N*-Aroyl Indoles

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1. General experimental information

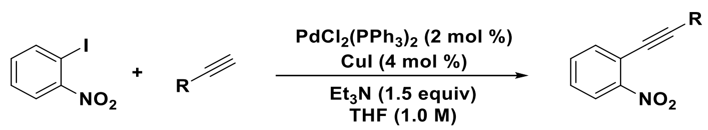
Unless otherwise noted, all reactions were carried out under nitrogen atmosphere. All commercially available reagents were used without further purification. All of the solvents were treated according to known methods. Column chromatography was performed on silica gel (200-400 mesh). ^{1}H NMR (400 MHz) chemical shifts were reported in ppm (*δ*) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard. ^{13}C NMR (101 MHz) chemical shifts were reported in ppm (*δ*) from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet), coupling constants (Hz) and integration. HRMS measurements were obtained on a TOF analyzer.

Special precaution on $Ni(CO)_4$ formation during the reaction should be taken!!!

2. General procedure for the synthesis of 2-nitroalkynes (1a–k)

The substrates **1a-e** and **1g-h** were prepared according to procedures described in the literature[4] reported before.

The 2-nitroalkynes **1f** and **1i-k** were prepared according to a general procedure reported by Shi.[1]



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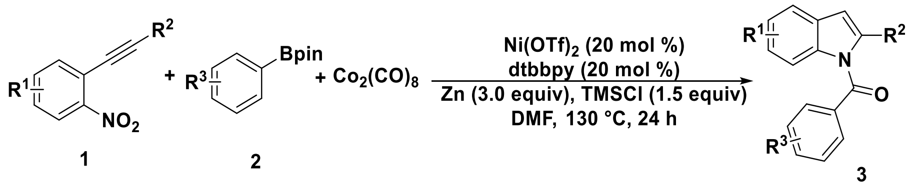
To a 50 mL flask charged with 1-iodo-2-nitrobenzene (5.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (70.2mg, 0.1 mmol, 2 mol%) and CuI (38.1 mg, 0.2 mmol, 4 mol%) in dry THF (5 mL) was added Et_3N (7.5 mmol, 1.5 equiv) and an alkyne (6.0 mmol, 1.2 equiv) under N_2 atmosphere and the resulting solution was stirred at room temperature overnight. Upon completion, the solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (3 × 5 mL), water (2 × 10 mL) and brine (10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica-gel column chromatography (petroleum ether / ethyl acetate = 30 / 1) to give the 2-nitroalkyne **1**.

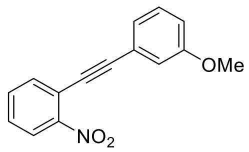
3. General procedure for the synthesis of indoles (3aa–aq and 3ba–ka)



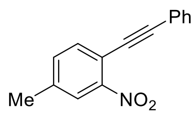
A 2-nitroalkyne **1** (0.4 mmol, 2.0 equiv), an aryl Bpin **2** (0.2 mmol, 1.0 equiv), $Ni(OTf)_2$ (14.3 mg, 0.04 mmol, 20 mol%), dtbbpy (10.7 mg, 0.04 mmol, 20 mol%), Zn (39.2 mg, 0.6 mmol, 3.0 equiv), TMSCl (32.6 mg, 0.3 mmol, 1.5 equiv), and $Co_2(CO)_8$ (68.4 mg, 0.2 mmol, 1.0 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. DMF (1.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 130 °C for 24 h. The resulting mixture was purified by silica-gel column chromatography (petroleum ether / ethyl acetate = 30 / 1) to obtain the indole **3**.

1 mmol scale: A 2-nitroalkyne **1a** (2 mmol, 2.0 equiv), an aryl Bpin **2a** (1 mmol, 1.0 equiv), $Ni(OTf)_2$ (20 mol%), dtbbpy (20 mol%), Zn (3.0 equiv), TMSCl (1.5 equiv), and $Co_2(CO)_8$ (1.0 equiv) were added to an oven-dried tube (15 mL). Then the tube was placed under vacuum and refilled with nitrogen three times. DMF (5.0 mL) were added into the tube via syringe. The tube was sealed and stirred at 130 °C for 24 h. The resulting mixture was purified by silica-gel column chromatography (petroleum ether / ethyl acetate = 30 / 1) to obtain the indole **3a** in 72% yield (213.9 mg).

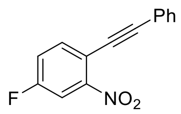
4. Characterization data of substrates 1f and 1i–k



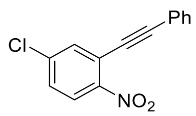
1-((3-methoxyphenyl)ethynyl)-2-nitrobenzene (1f).[2] Yellow solid in 76% yield; mp 39.7 – 41.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.49 – 7.44 (m, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.13 – 7.09 (m, 1H), 6.96 – 6.93 (m, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 149.6, 134.7, 133.0, 129.7, 128.7, 124.9, 124.7, 123.4, 118.8, 116.6, 116.1, 97.1, 84.7, 55.5.



4-methyl-2-nitro-1-(phenylethynyl)benzene (1i).[3] Yellow solid in 59% yield; mp 41.9 – 43.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.60 – 7.57 (m, 3H), 7.40 – 7.35 (m, 4H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 139.7, 134.4, 133.8, 132.0, 129.1, 128.5, 125.1, 122.7, 115.9, 96.2, 85.0, 21.3.

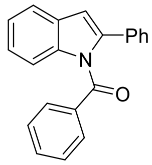


4-fluoro-2-nitro-1-(phenylethynyl)benzene (1j).[3] Yellow solid in 73% yield; mp 56.5 – 59.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 8.3, 2.6 Hz, 1H), 7.70 (dd, J = 8.6, 5.5 Hz, 1H), 7.59 – 7.57 (m, 2H), 7.39 – 7.31 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, J = 254.3 Hz, 1C), 150.2 (d, J = 8.2 Hz, 1C), 136.2 (d, J = 8.0 Hz, 1C), 132.0, 129.4, 128.6, 122.3, 120.8 (d, J = 21.9 Hz, 1C), 115.2 (d, J = 3.8 Hz, 1C), 112.6 (d, J = 27.0 Hz, 1C), 97.1 (d, J = 1.5 Hz, 1C), 83.9.

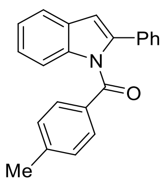


4-chloro-1-nitro-2-(phenylethynyl)benzene (1k).[3] Yellow solid in 68% yield; mp 60.4 – 62.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 1.5 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.43 – 7.36 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 139.4, 134.1, 132.2, 129.7, 128.7, 128.6, 126.2, 121.9, 120.5, 98.7, 84.0.

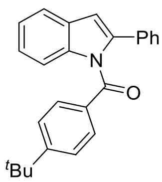
5. Characterization data of products 3aa–aq, 3ba–ka, and 4



phenyl(2-phenyl-1*H*-indol-1-yl)methanone (3aa).[4] Yellow solid, 41.6 mg, 70% yield, mp 107.9 – 109.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.32 – 7.24 (m, 6H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.15 – 7.11 (m, 1H), 6.79 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 141.4, 138.3, 135.2, 133.1, 132.9, 130.4, 129.4, 128.5, 128.4, 128.3, 127.7, 124.3, 123.2, 120.8, 114.2, 109.6.

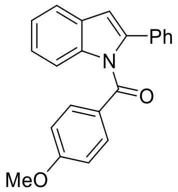


(2-phenyl-1*H*-indol-1-yl)(*p*-tolyl)methanone (3ab).[4] Yellow solid, 35.5 mg, 57% yield, mp 143.7 – 146.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.63 (m, 1H), 7.58 (d, *J* = 8.1 Hz, 3H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.28 – 7.20 (m, 4H), 7.18 – 7.14 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.79 (s, 1H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 144.0, 141.5, 138.3, 133.1, 132.3, 130.6, 129.4, 129.2, 128.3, 127.6, 124.1, 123.0, 120.8, 114.0, 109.2, 21.8.

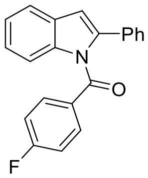


(4-(*tert*-butyl)phenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ac).[4] Yellow oil, 36.8 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 1H), 7.69 – 7.65 (m, 1H), 7.61 – 7.59 (m, 2H), 7.33 – 7.27 (m, 6H), 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 1H), 6.80 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (101

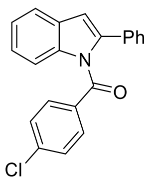
MHz, $CDCl_3$) δ 170.1, 156.7, 141.5, 138.4, 133.2, 132.2, 130.4, 129.4, 128.5, 128.2, 127.5, 125.3, 124.2, 123.1, 120.8, 114.2, 109.3, 35.2, 31.1.



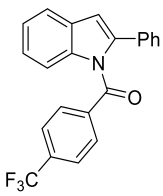
(4-methoxyphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ad).[4] Yellow oil, 44.5 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 3H), 7.56 (dd, J = 6.7, 2.4 Hz, 1H), 7.36 – 7.34 (m, 2H), 7.27 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 6,80 – 6.77 (m, 3H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 163.6, 141.5, 138.4, 133.1, 132.9, 129.3, 128.4, 128.3, 127.7, 127.3, 124.0, 122.8, 120.8, 113.9, 113.8, 108.8, 55.6.



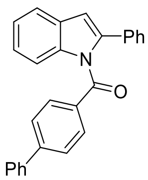
(4-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ae).[4] Yellow oil, 39.1 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.75 (m, 1H), 7.67 – 7.61 (m, 3H), 7.32 – 7.28 (m, 4H), 7.22 – 7.13 (m, 3H), 6.95 – 6.89 (m, 2H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 168.9, 165.4 (d, J = 255.2 Hz, 1C), 141.1, 138.3, 132.9 (d, J = 9.4 Hz, 1C), 131.4 (d, J = 3.0 Hz, 1C), 129.3, 128.45, 128.40, 127.8, 124.5 123.4, 120.9, 115.6 (d, J = 22.2 Hz, 1C), 114.1, 109.6.



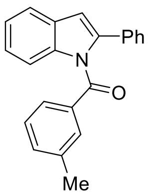
(4-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3af).[4] Yellow oil, 35.2 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.77 (m, 1H), 7.67 – 7.64 (m, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.32 – 7.28 (m, 4H), 7.23 – 7.17 (m, 5H), 6.80 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 141.1, 139.2, 138.2, 133.6, 132.9, 131.7, 129.4, 128.7, 128.5, 128.4, 127.9, 124.6, 123.5, 120.9, 114.2, 109.8.



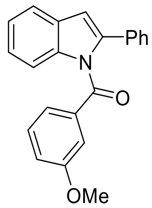
(2-phenyl-1*H*-indol-1-yl)(4-(trifluoromethyl)phenyl)methanone (3ag).[4] Yellow solid, 40.9 mg, 56% yield, mp 110.6 – 113.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 1H), 7.67 – 7.64 (m, 3H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.24 – 7.22 (m, 2H), 7.17 – 7.09 (m, 3H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 140.9, 138.6, 138.2, 133.8 (q, *J* = 32.8 Hz, 1C), 132.9, 130.4, 129.4, 128.7, 128.4, 127.9, 125.2 (q, *J* = 3.6 Hz, 1C), 124.9, 123.8, 123.5 (q, *J* = 272.8 Hz, 1C), 121.0, 114.5, 110.4.



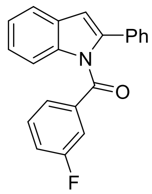
[1,1'-biphenyl]-4-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ah).[4] Yellow oil, 46.3 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 3H), 7.68 – 7.66 (m, 1H), 7.55 – 7.44 (m, 6H), 7.42 – 7.38 (m, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 6.82 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 145.6, 141.4, 139.8, 138.3, 133.8, 133.1, 131.0, 129.4, 129.1, 128.5, 128.4, 128.3, 127.7, 127.3, 127.0, 124.3, 123.2, 120.9, 114.2, 109.5.



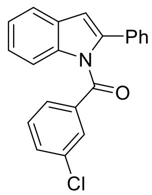
(2-phenyl-1*H*-indol-1-yl)(*m*-tolyl)methanone (3ai).[4] Yellow oil, 41.7 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.70 (m, 1H), 7.67 – 7.64 (m, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (s, 1H), 7.33 – 7.25 (m, 4H), 7.22 – 7.12 (m, 5H), 6.79 (s, 1H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 170.3, 141.4, 138.4, 138.1, 135.0, 133.7, 133.3, 131.0, 129.3, 128.4, 128.2, 127.6, 124.3, 123.2, 120.8, 114.2, 109.5, 21.2.



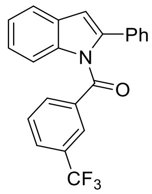
(3-methoxyphenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3aj).[5] Yellow oil, 36.0 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.23 – 7.13 (m, 6H), 6.94 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.79 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 159.4, 141.4, 138.3, 136.4, 133.2, 129.5, 129.4, 128.34, 128.29, 127.7, 124.3, 123.2, 123.0, 120.8, 119.6, 114.6, 114.2, 109.6, 55.5.



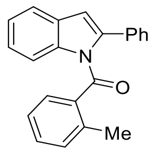
(3-fluorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3ak).[4] Yellow oil, 45.4 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 1H), 7.66 (dd, *J* = 5.9, 2.8 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.34 – 7.26 (m, 5H), 7.21 – 7.12 (m, 4H), 7.05 (td, *J* = 8.3, 1.7 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 162.2 (d, *J* = 248.3 Hz, 1C), 141.0, 138.3, 137.4 (d, *J* = 7.1 Hz, 1C), 133.0, 130.0 (d, *J* = 7.8 Hz, 1C), 129.4, 128.5, 128.4, 127.8, 126.0 (d, *J* = 2.9 Hz, 1C), 124.7, 123.6, 120.9, 119.7 (d, *J* = 21.3 Hz, 1C), 117.1 (d, *J* = 23.2 Hz, 1C), 114.3, 110.0.



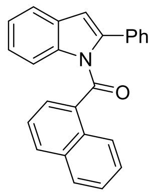
(3-chlorophenyl)(2-phenyl-1*H*-indol-1-yl)methanone (3al).[4] Yellow oil, 34.5 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.67 – 7.65 (m, 1H), 7.50 – 7.46 (m, 2H), 7.33 – 7.26 (m, 5H), 7.21 – 7.11 (m, 4H), 6.78 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 141.0, 138.3, 136.9, 134.3, 133.0, 132.5, 130.3, 129.6, 129.4, 128.5, 128.4, 128.3, 127.9, 124.8, 123.7, 120.9, 114.4, 110.1.



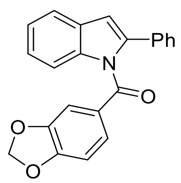
(2-phenyl-1*H*-indol-1-yl)(3-(trifluoromethyl)phenyl)methanone (3am).[5] Yellow oil, 37.3 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.24 – 7.22 (m, 2H), 7.15 – 7.06 (m, 3H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 140.7, 138.3, 136.2, 133.2, 132.9, 130.6 (q, J = 33.1 Hz, 1C), 129.4, 128.9, 128.8 (q, J = 3.6 Hz, 1C), 128.7, 128.4, 127.9, 127.1 (q, J = 3.5 Hz, 1C), 125.0, 123.9, 123.4 (q, J = 272.4 Hz, 1C), 121.0, 114.5, 110.4.



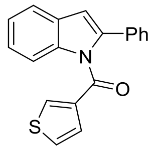
(2-phenyl-1*H*-indol-1-yl)(*o*-tolyl)methanone (3an).[4] Yellow oil, 26.2 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.72 (m, 1H), 7.66 – 7.62 (m, 1H), 7.32 – 7.27 (m, 4H), 7.22 – 7.13 (m, 5H), 7.07 (d, J = 7.9 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.73 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.2, 138.1, 138.0, 135.6, 133.4, 131.5, 131.1, 129.8, 129.5, 128.4, 128.0, 127.7, 125.6, 124.7, 123.5, 120.8, 114.5, 110.5, 19.8.



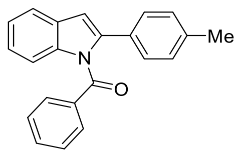
naphthalen-1-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ao).[5] Yellow oil, 42.3 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.74 – 7.72 (m, 2H), 7.66 – 7.64 (m, 1H), 7.52 – 7.44 (m, 3H), 7.33 – 7.21 (m, 2H), 7.21 (t, J = 7.7 Hz, 1H), 7.08 – 7.06 (m, 2H), 6.88 – 6.85 (m, 3H), 6.69 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 141.5, 138.2, 133.4, 133.2, 133.0, 132.4, 131.0, 129.5, 129.3, 128.4, 128.3, 127.8, 127.6, 127.3, 126.5, 125.1, 124.8, 124.3, 123.7, 120.8, 115.1, 110.5.



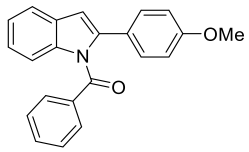
benzo[*d*][1,3]dioxol-5-yl(2-phenyl-1*H*-indol-1-yl)methanone (3ap). Yellow oil, 41.6 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.31 (d, J = 7.2 Hz, 2H), 7.23 – 7.13 (m, 7H), 6.75 (s, 1H), 6.63 (d, J = 8.1 Hz, 1H), 5.95 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 151.9, 147.9, 141.4, 138.4, 133.1, 129.3, 129.0, 128.4, 128.2, 127.7, 127.0, 124.1, 123.0, 120.9, 113.9, 110.3, 109.0, 108.0, 102.0; HRMS (ESI-TOF) Calcd. for $C_{22}H_{16}NO_3^+$ $[M+H]^+$: 342.1125; found: 342.1127.



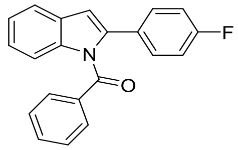
(2-phenyl-1*H*-indol-1-yl)(thiophen-3-yl)methanone (3aq).[5] Yellow oil, 33.4 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.80 (m, 1H), 7.72 (dd, J = 3.0, 1.2 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.35 – 7.28 (m, 5H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 1H), 7.12 (dd, J = 5.1, 3.0 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 140.9, 138.3, 137.8, 134.5, 133.2, 129.2, 128.5, 128.4, 128.2, 127.7, 126.2, 124.4, 123.2, 120.9, 114.0, 109.5.



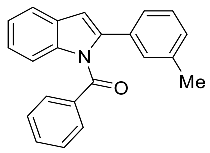
phenyl(2-(*p*-tolyl)-1*H*-indol-1-yl)methanone (3ba).[4] Yellow solid, 36.1 mg, 58% yield, mp 114.3 – 117.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 4H), 7.53 (t, J = 7.5 Hz, 1H), 7.40 – 7.30 (m, 6H), 7.11 (d, J = 7.9 Hz, 2H), 6.85 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.6, 138.2, 137.5, 135.2, 132.9, 130.4, 130.2, 129.5, 129.0, 128.4, 128.3, 124.1, 123.1, 120.7, 114.1, 109.1, 21.3.



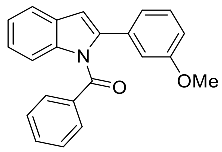
(2-(4-methoxyphenyl)-1*H*-indol-1-yl)(phenyl)methanone (3ca).[4] Yellow oil, 35.4 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 4H), 7.43 – 7.39 (m, 1H), 7.29 – 7.21 (m, 6H), 6.75 – 6.71 (m, 3H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 159.1, 141.2, 138.2, 135.2, 133.0, 130.4, 129.7, 129.5, 128.4, 125.7, 124.0, 123.1, 120.6, 114.1, 113.8, 55.4.



(2-(4-fluorophenyl)-1*H*-indol-1-yl)(phenyl)methanone (3da).[4] Yellow solid, 37.8 mg, 60% yield, mp 117.9 – 120.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 4H), 7.46 – 7.42 (m, 1H), 7.31 – 7.24 (m, 6H), 6.92 – 6.86 (m, 2H), 6.75 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 162.2 (d, J = 248.1 Hz, 1C), 140.2, 138.2, 135.1, 133.1, 130.3, 130.1 (d, J = 8.2 Hz, 1C), 129.4 (d, J = 3.3 Hz, 1C), 129.3, 128.5, 124.4, 123.3, 120.8, 115.4 (d, J = 21.8 Hz, 1C), 114.2, 109.7.

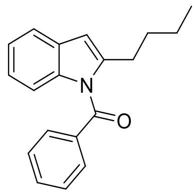


phenyl(2-(*m*-tolyl)-1*H*-indol-1-yl)methanone (3ea).[4] Yellow solid, 33.0 mg, 53% yield, mp 102.7 – 105.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.69 (m, 1H), 7.66 – 7.60 (m, 3H), 7.39 (t, J = 7.4 Hz, 1H), 7.29 – 7.23 (m, 5H), 7.12 – 7.04 (m, 3H), 6.92 (d, J = 7.4 Hz, 1H), 6.77 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.5, 138.3, 137.8, 135.4, 133.0, 132.8, 130.2, 129.4, 129.3, 128.4, 128.3, 128.2, 125.6, 124.3, 123.2, 120.8, 114.2, 109.4, 21.4.

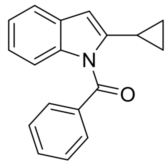


(2-(3-methoxyphenyl)-1*H*-indol-1-yl)(phenyl)methanone (3fa). Yellow oil, 41.9 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 1H), 7.66 – 7.62 (m, 3H), 7.42 – 7.39 (m, 1H), 7.30 –

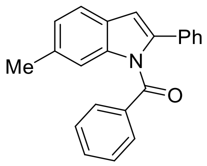
7.25 (m, 4H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.85 – 6.84 (m, 1H), 6.79 (s, 1H), 6.69 – 6.66 (m, 1H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 159.2, 141.1, 138.3, 135.2, 134.4, 132.9, 130.3, 129.4, 129.3, 128.3, 124.4, 123.3, 121.1, 120.9, 114.2, 114.0, 113.4, 109.6, 55.3; HRMS (ESI-TOF) Calcd. for $C_{22}H_{18}NO_2^+$ $[M+H]^+$: 328.1332; found: 328.1334.



(2-butyl-1*H*-indol-1-yl)(phenyl)methanone (3ga).[5] Yellow oil, 34.9 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.97 (m, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.48 (s, 1H), 2.86 – 2.82 (m, 2H), 1.66 – 1.57 (m, 2H), 1.39 – 1.26 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 143.2, 137.4, 135.6, 133.2, 130.0, 129.6, 128.9, 122.6, 122.5, 120.1, 114.2, 107.4, 31.3, 28.7, 22.5, 14.0.

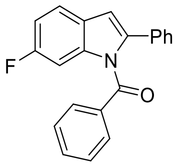


(2-cyclopropyl-1*H*-indol-1-yl)(phenyl)methanone (3ha).[5] Yellow oil, 30.3 mg, 58% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.33 (s, 1H), 1.84 – 1.78 (m, 1H), 0.76 – 0.66 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 144.4, 137.5, 136.0, 132.8, 129.9, 129.3, 128.7, 123.3, 122.8, 120.1, 114.4, 106.0, 10.4, 8.5.

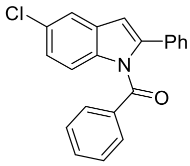


(6-methyl-2-phenyl-1*H*-indol-1-yl)(phenyl)methanone (3ia).[6] Yellow oil, 38.6 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.60 – 7.58 (m, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.21 (m, 4H), 7.18 – 7.08 (m, 4H), 6.73 (s, 1H), 2.46 (s, 3H); ^{13}C NMR (101

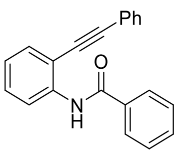
MHz, $CDCl_3$) δ 170.3, 140.6, 138.8, 135.3, 134.5, 133.3, 132.8, 130.3, 128.4, 128.2, 127.4, 127.1, 124.8, 120.4, 114.4, 109.4, 22.1.



(6-fluoro-2-phenyl-1*H*-indol-1-yl)(phenyl)methanone (3ja). Yellow oil, 27.1 mg, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 3H), 7.48 (d, J = 10.3 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H), 7.27 – 7.22 (m, 4H), 7.16 (t, J = 7.4 Hz, 2H), 7.13 – 7.09 (m, 1H), 7.04 (t, J = 8.4 Hz, 1H), 6.73 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 160.9 (d, J = 240.5 Hz, 1C), 141.7 (d, J = 4.2 Hz, 1C), 138.5 (d, J = 12.4 Hz, 1C), 134.8, 133.1, 132.9, 130.3, 128.4, 128.3 (d, J = 0.7 Hz, 1C), 127.7, 125.6, 121.5 (d, J = 9.8 Hz, 1C), 111.7 (d, J = 24.2 Hz, 1C), 109.1, 101.6 (d, J = 28.4 Hz, 1C); HRMS (ESI-TOF) Calcd. for $C_{21}H_{14}NFONa^+$ $[M+Na]^+$: 338.0952; found: 338.0954.



(5-chloro-2-phenyl-1*H*-indol-1-yl)(phenyl)methanone (3ia).[6] Yellow solid, mp 95.1 – 96.5 °C; 33.8 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.8 Hz, 1H), 7.61 – 7.58 (m, 3H), 7.39 (t, J = 7.5 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.23 – 7.11 (m, 4H), 6.71 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 142.6, 136.7, 134.8, 133.1, 132.6, 130.4, 130.3, 128.7, 128.5, 128.44, 128.37, 128.0, 124.5, 120.3, 115.2, 108.5.



***N*-(2-(phenylethynyl)phenyl)benzamide (4).[7]** White solid, 93% yield. mp 113.6 – 115.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.64 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 7.5 Hz, 2H), 7.59 – 7.48 (m, 6H), 7.45 – 7.40 (m, 4H), 7.13 (t, J = 7.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 139.2, 135.1, 132.2, 131.7, 131.5, 130.1, 129.14, 129.05, 128.8, 127.1, 123.7, 122.4, 119.3, 112.4, 97.1, 84.6

6. References

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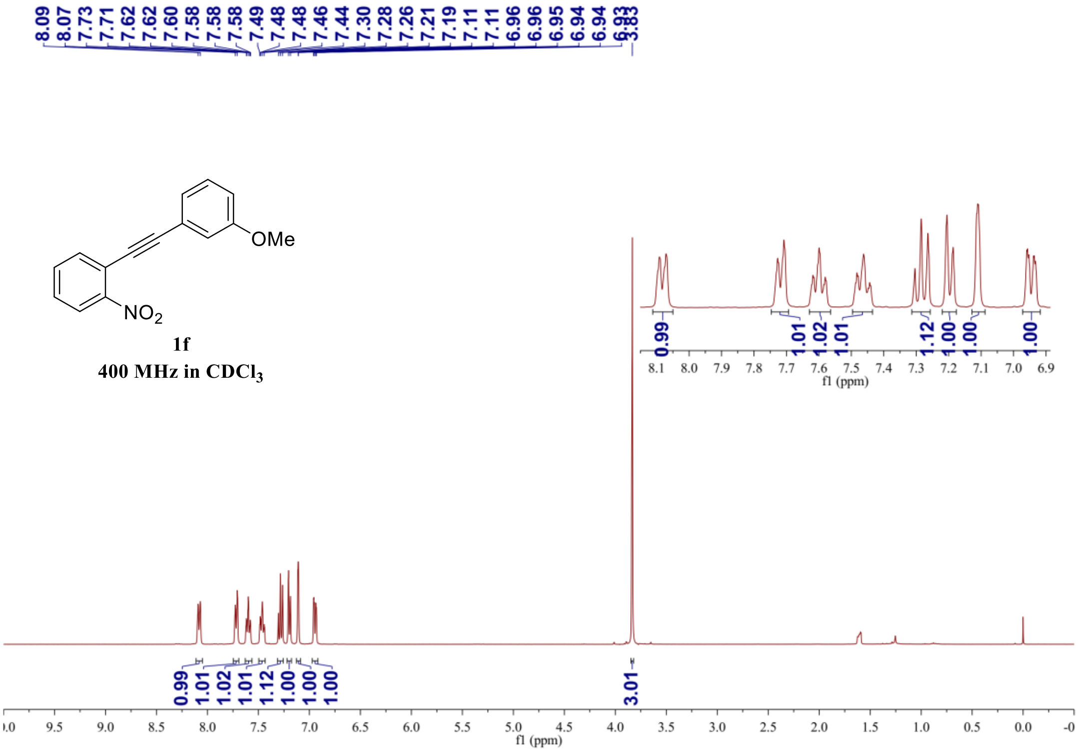
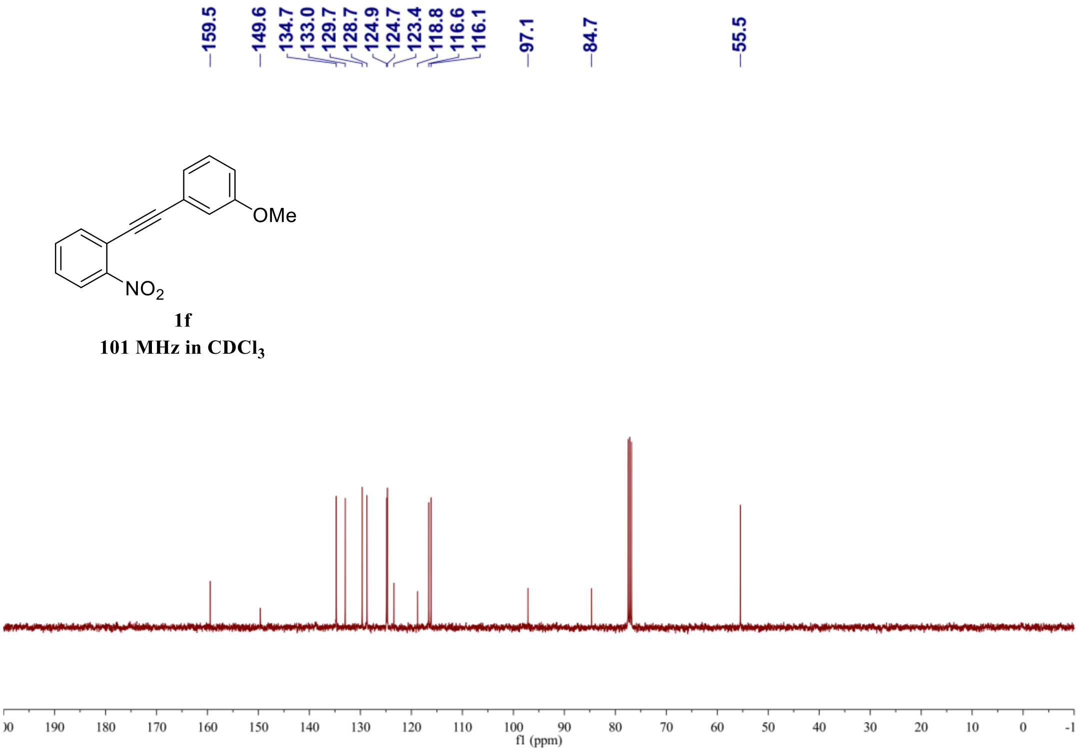
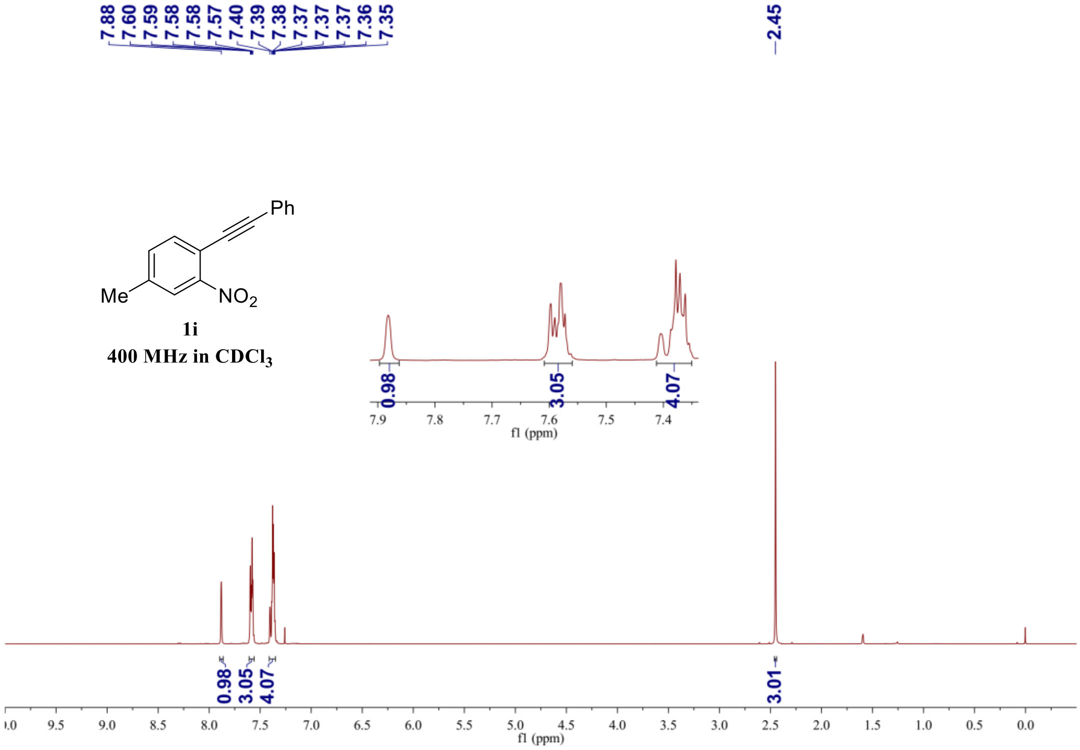
7. ^{1}H, ^{13}C NMR spectra of 1f, 1i–k, 3aa–aq, 3ba–ka and 4



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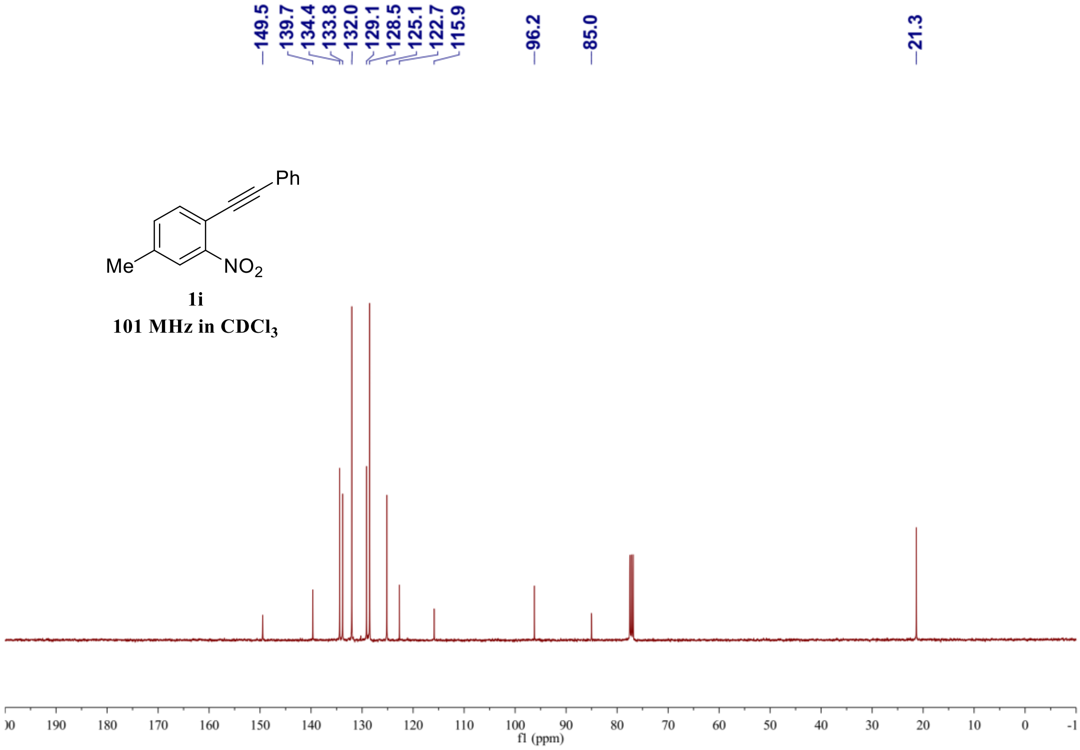
2.45
Ph
Me
NO_2
1i
400 MHz in $CDCl_3$
0.98
3.05
4.07
3.01
f1 (ppm)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96.2
85.0
21.3
Ph
Me
NO_2
1i
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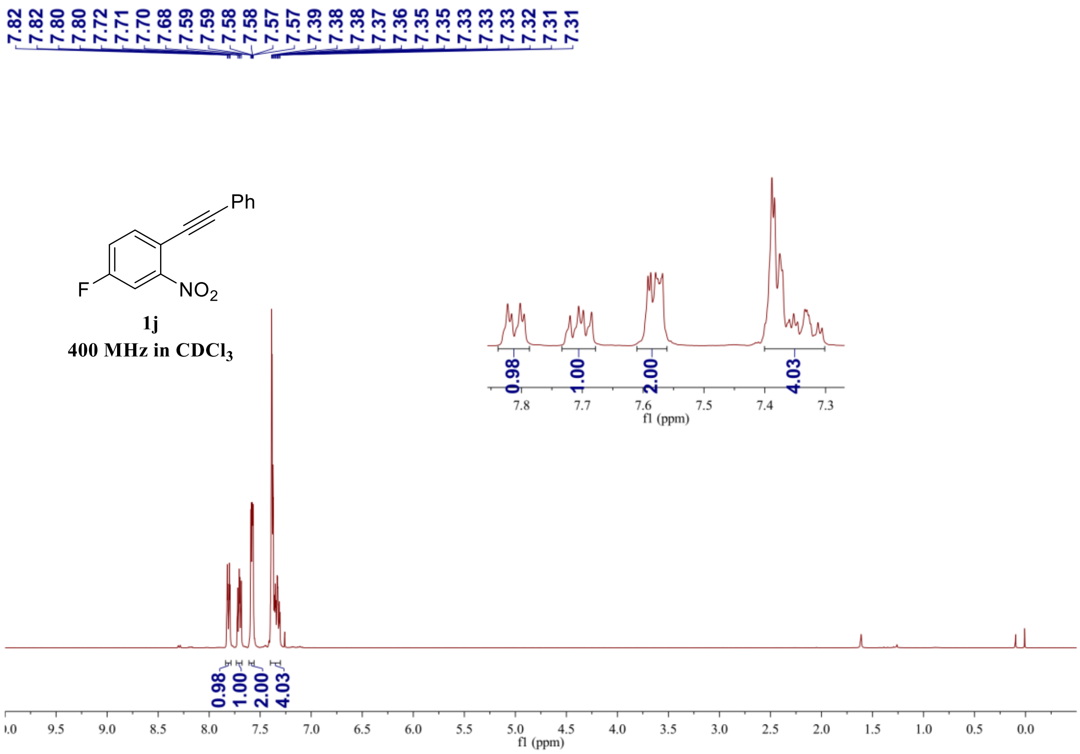
f1 (ppm)



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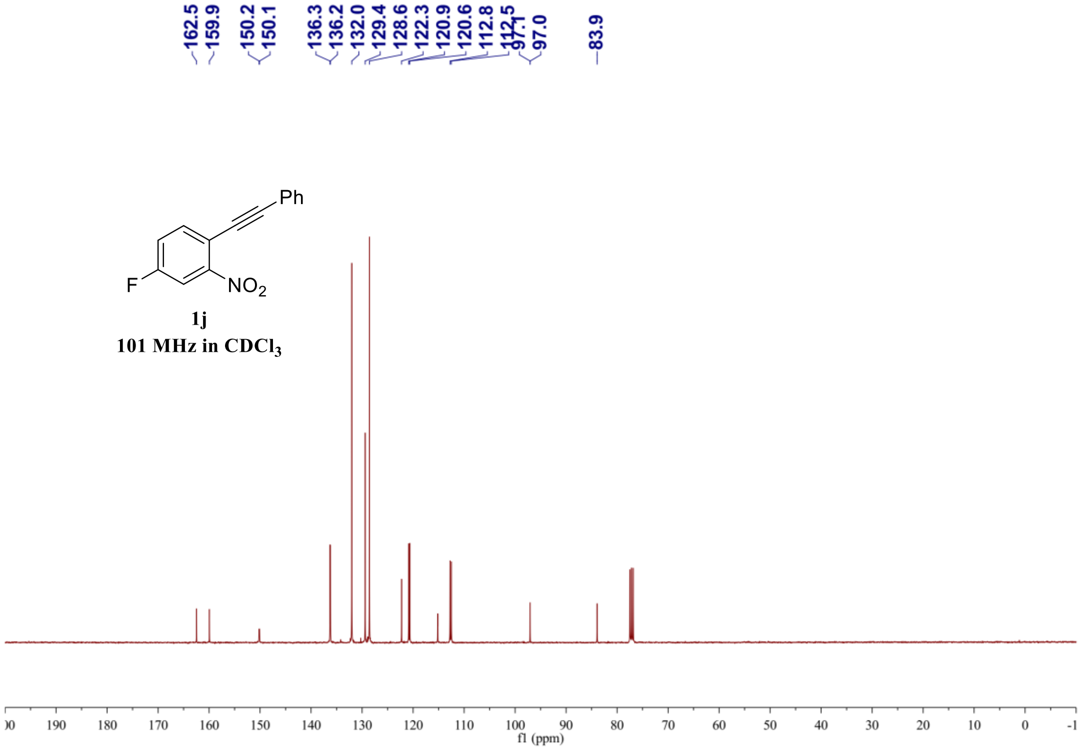
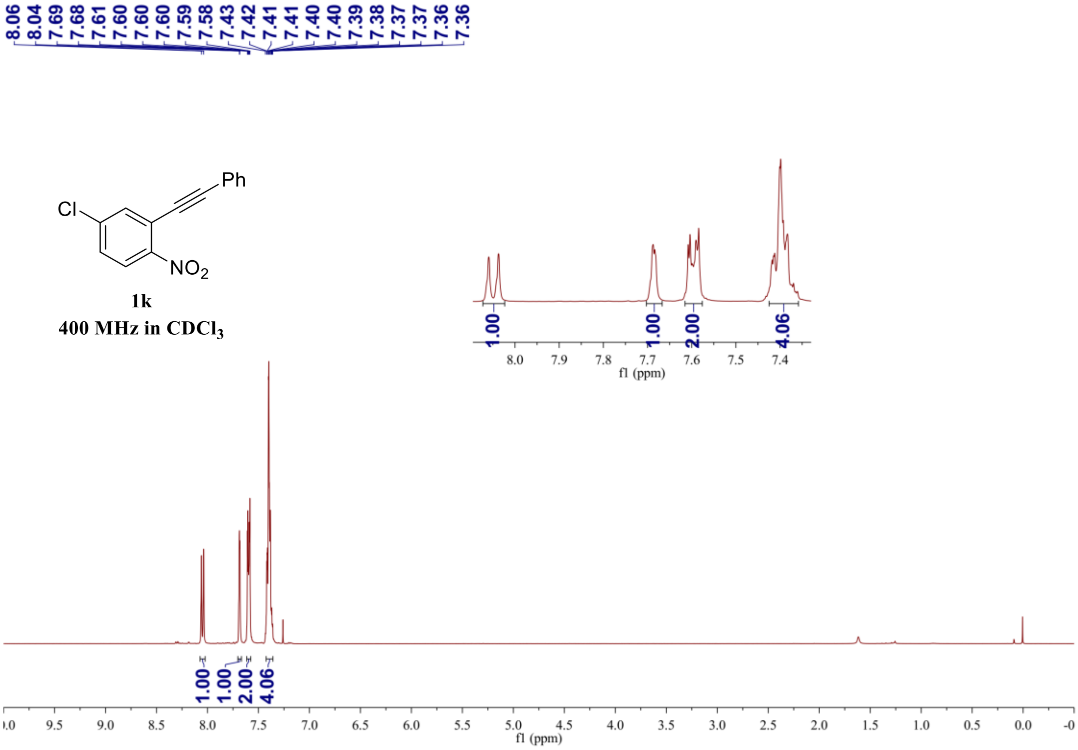
Ph
F
NO2
1j
400 MHz in CDCl3
0.98
1.00
2.00
4.03
f1 (ppm)



162.5 159.9 150.2 150.1 136.3 136.2 132.0 129.4 128.6 122.3 120.9 120.6 112.8 112.5 97.1 97.0 83.9
Ph
F
NO2
1j
101 MHz in CDCl3
f1 (ppm)



1k
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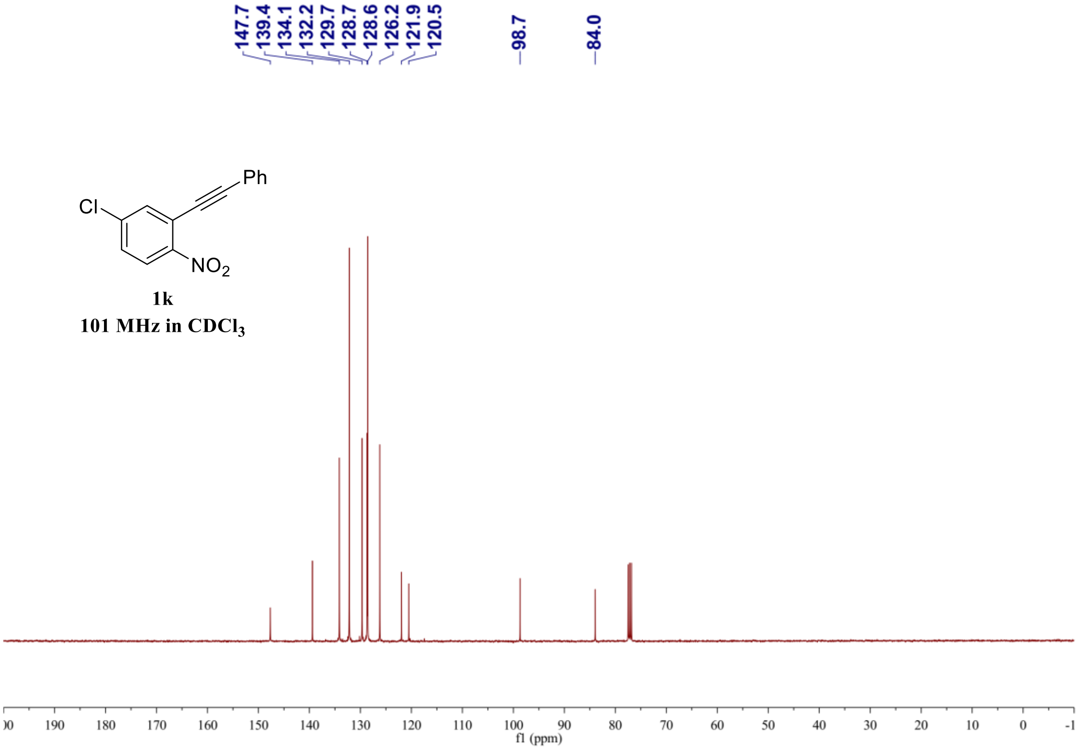
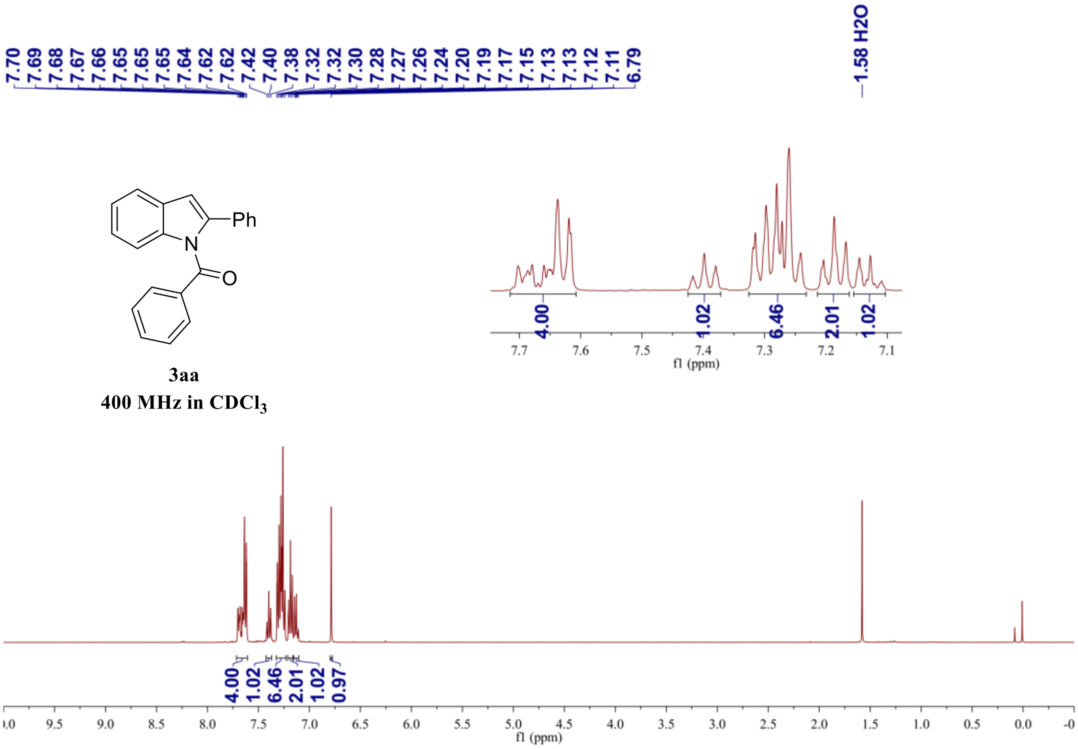


1k
101 MHz in $CDCl_3$



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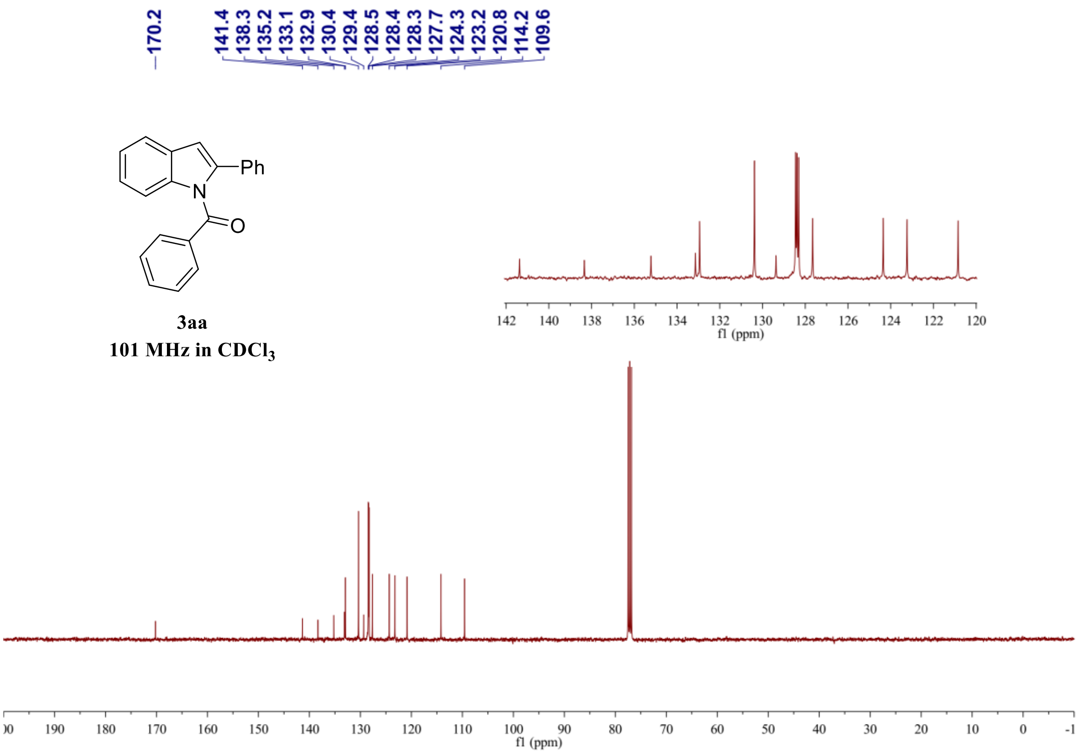
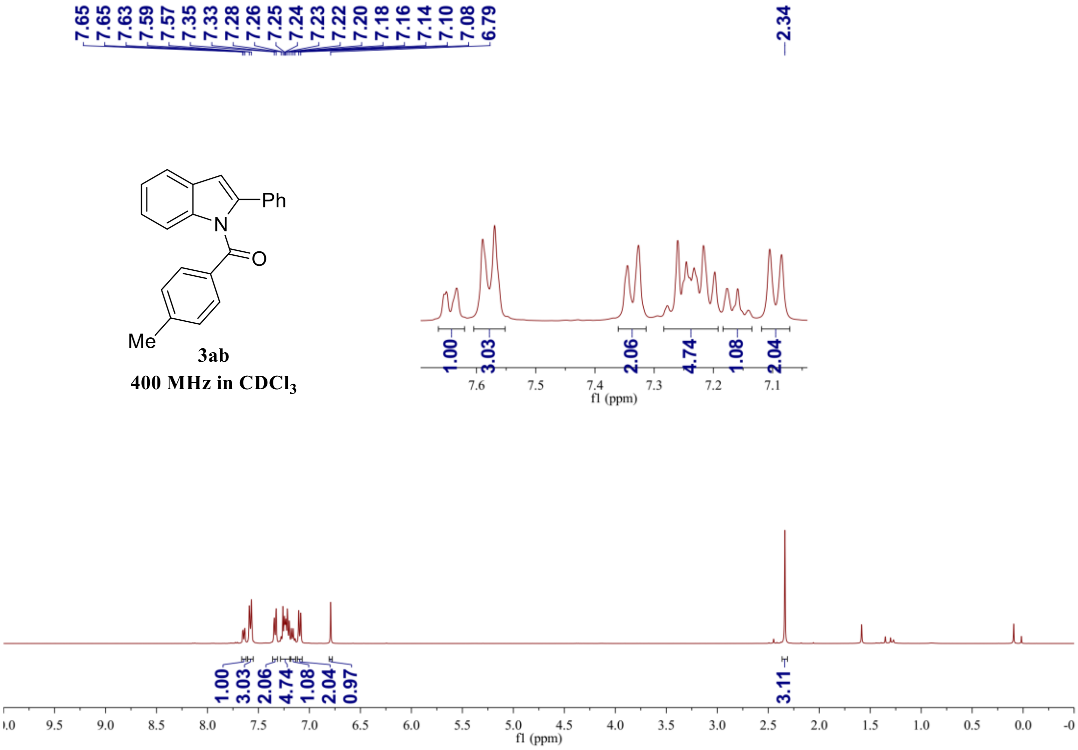


3aa
101 MHz in $CDCl_3$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7.22
7.20
7.18
7.16
7.14
7.10
7.08
6.79
2.34
Ph
N
O
Me
3ab
400 MHz in $CDCl_3$
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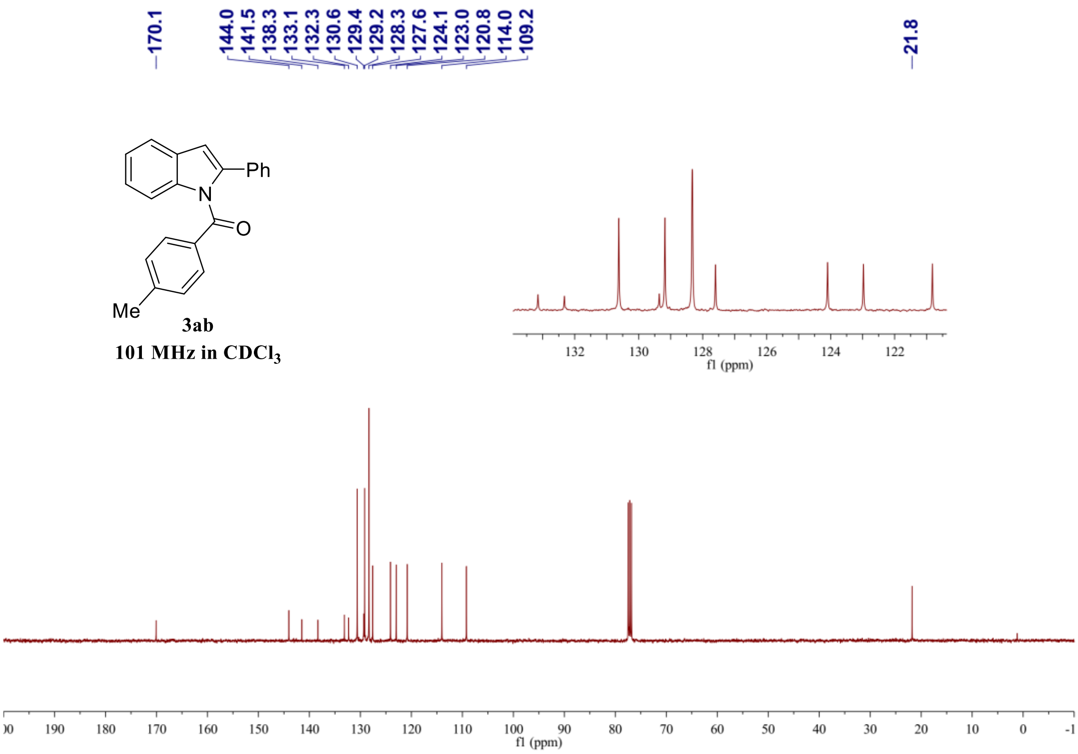
2.04
0.97
3.11
f1 (ppm)


170.1
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138.3
133.1
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129.4
129.2
128.3
127.6
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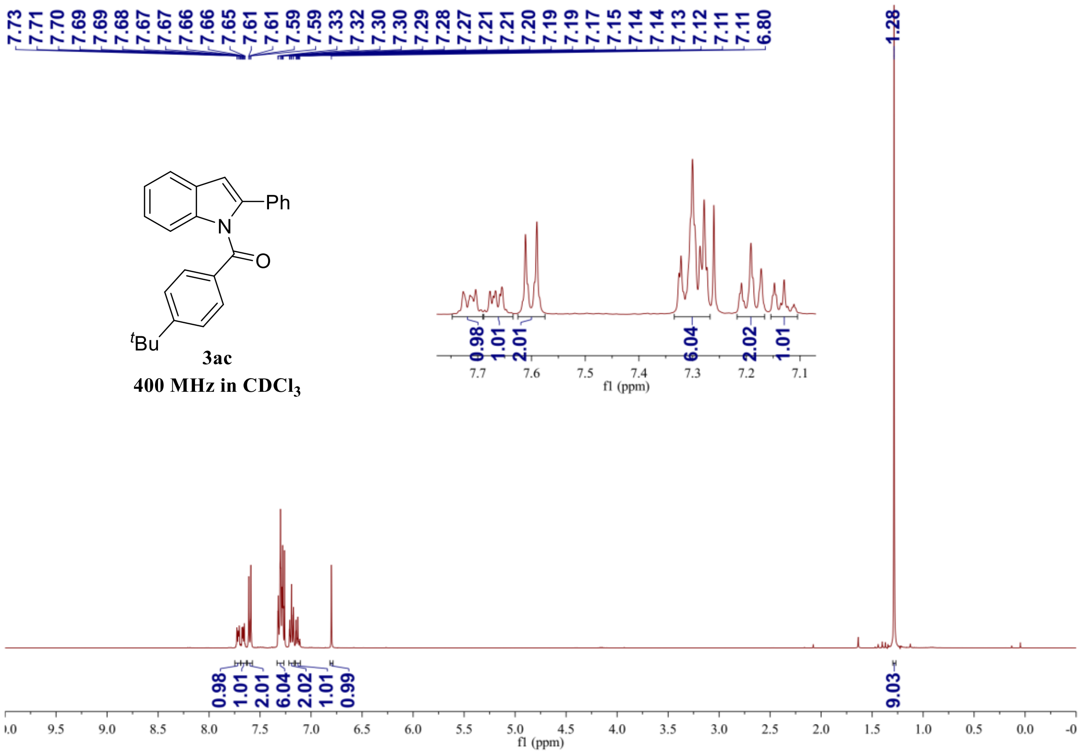
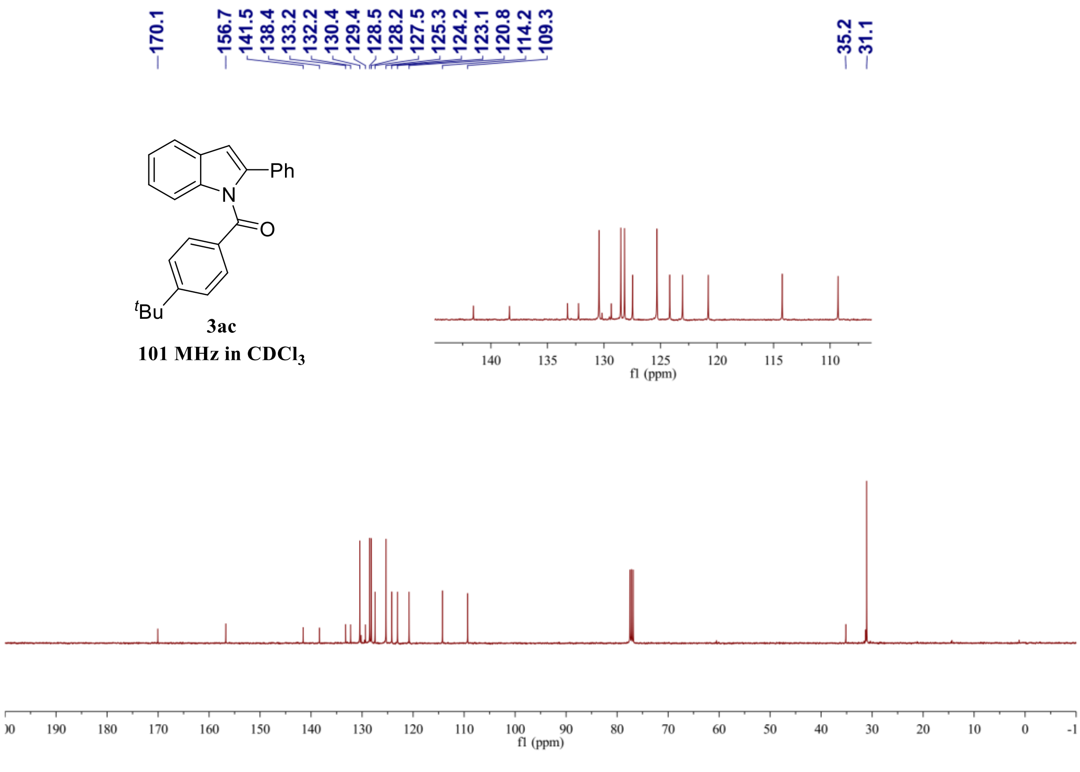
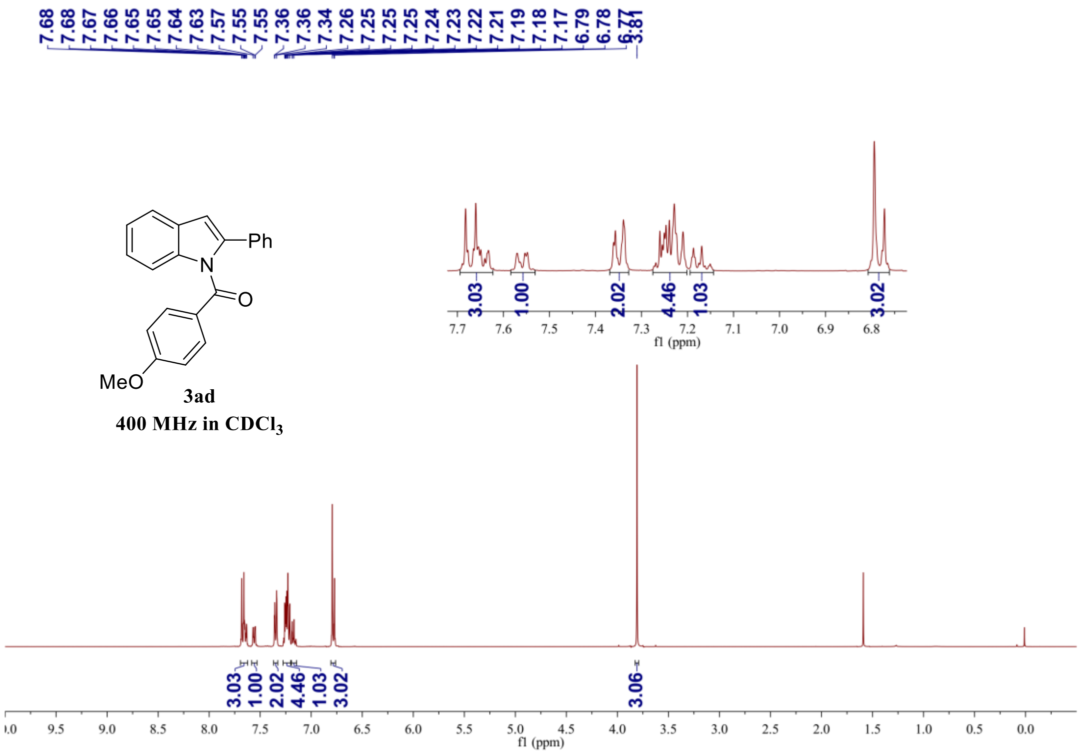
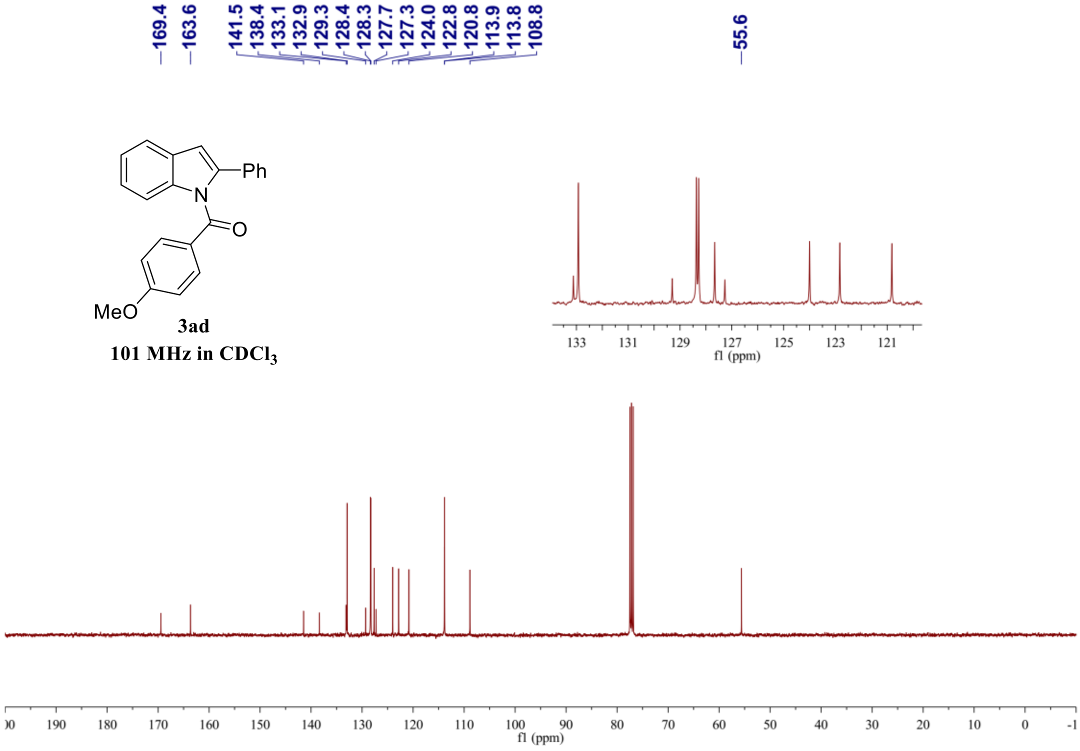
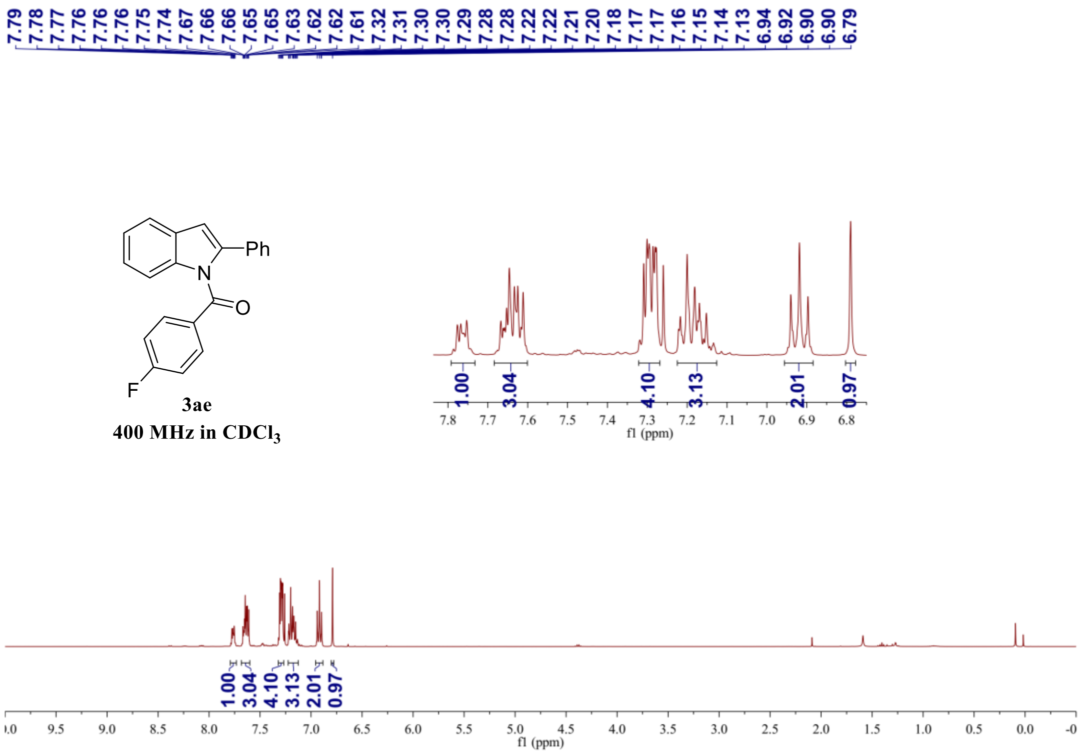
123.0
120.8
114.0
109.2
21.8
Ph
N
O
Me
3ab
101 MHz in $CDCl_3$
f1 (ppm)

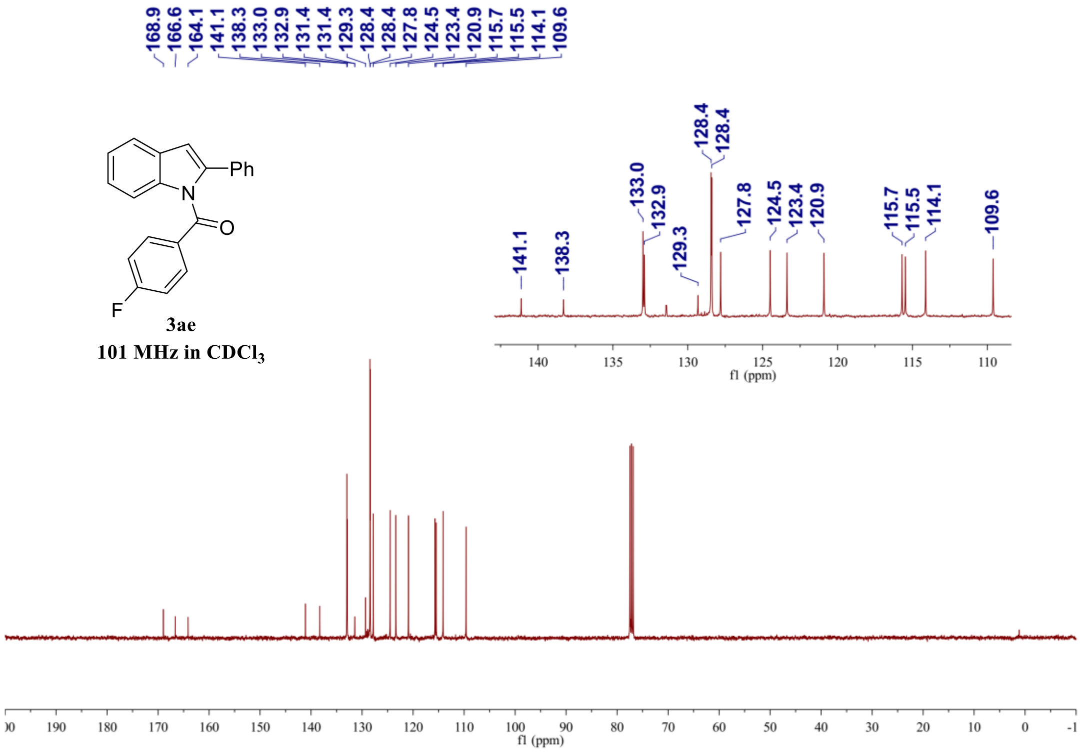

7.73 7.71 7.70 7.69 7.68 7.67 7.67 7.66 7.65 7.61 7.61 7.59 7.33 7.32 7.30 7.30 7.29 7.28 7.27 7.21 7.21 7.20 7.19 7.19 7.17 7.15 7.14 7.14 7.13 7.12 7.11 7.11 6.80
1.28
Ph
N
O
tBu
3ac
400 MHz in CDCl3
0.98 1.01 2.01 6.04 2.02 1.01 0.99
9.03
f1 (ppm)

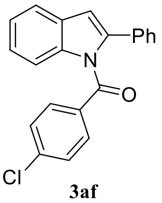

170.1
156.7 141.5 138.4 133.2 132.2 130.4 129.4 128.5 128.2 127.5 125.3 124.2 123.1 120.8 114.2 109.3
35.2 31.1
Ph
N
O
tBu
3ac
101 MHz in CDCl3
f1 (ppm)


7.68 7.68 7.67 7.66 7.65 7.64 7.63 7.57 7.55 7.55 7.36 7.36 7.34 7.26 7.25 7.25 7.25 7.24 7.23 7.22 7.21 7.19 7.18 7.17 6.79 6.78 6.77 3.81
Ph
N
O
MeO
3ad
400 MHz in CDCl3
3.03 1.00 2.02 4.46 1.03 3.02
3.06
f1 (ppm)


169.4 163.6 141.5 138.4 133.1 132.9 129.3 128.4 128.3 127.7 127.3 124.0 122.8 120.8 113.9 113.8 108.8 55.6
Ph
N
O
MeO
3ad
101 MHz in CDCl3
f1 (ppm)

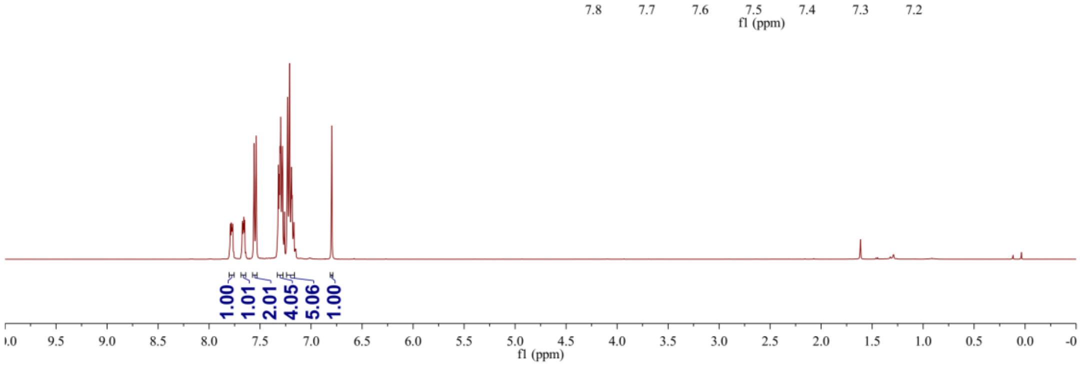

3ae
400 MHz in CDCl$_3$

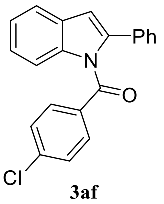

3ae
101 MHz in CDCl$_3$



3af

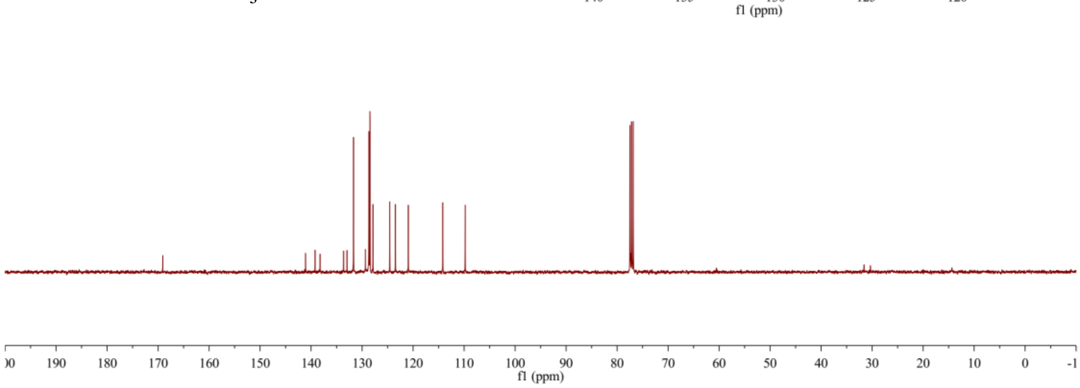
400 MHz in $CDCl_3$

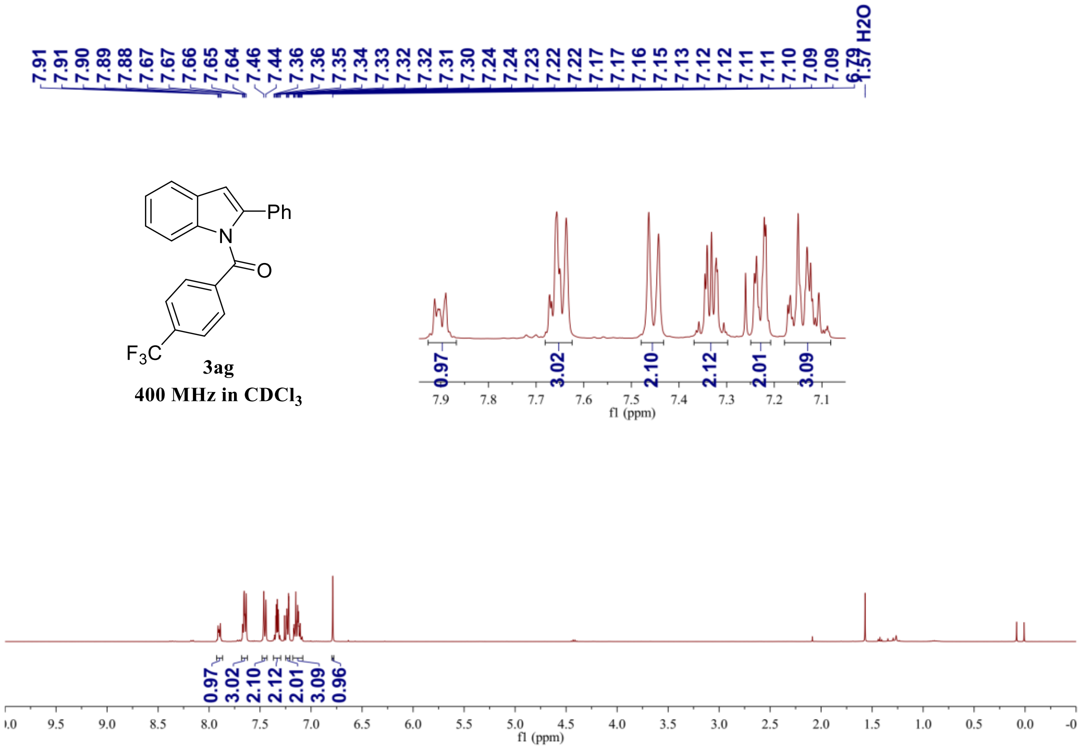


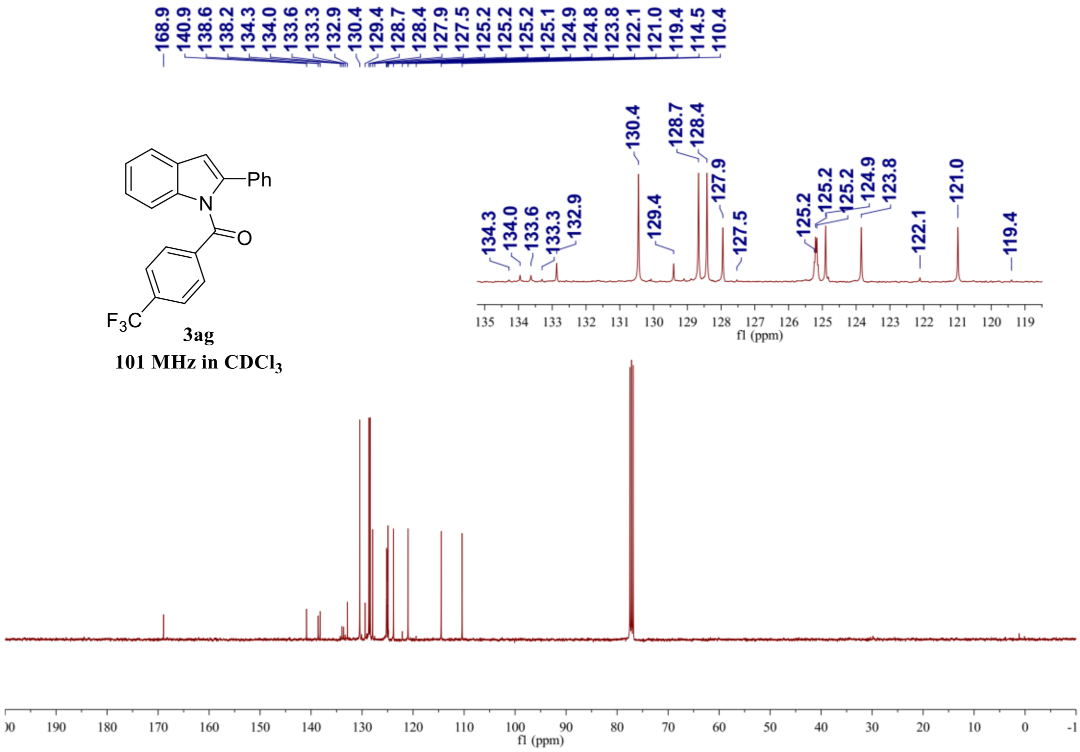


3af

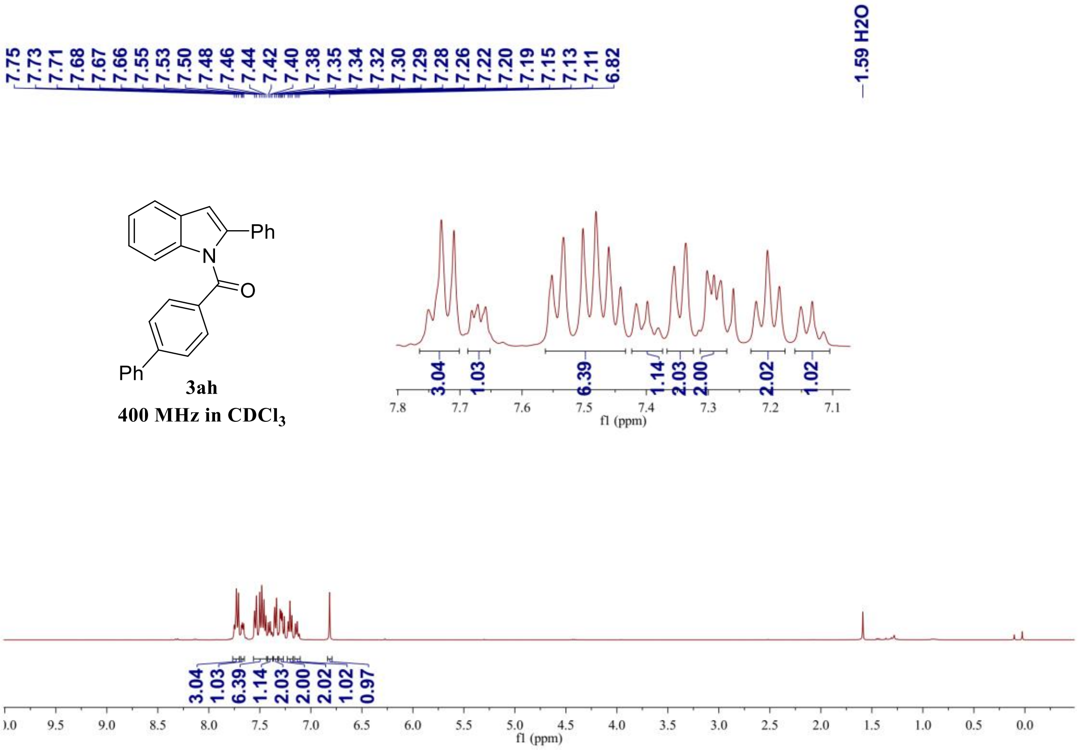
101 MHz in $CDCl_3$



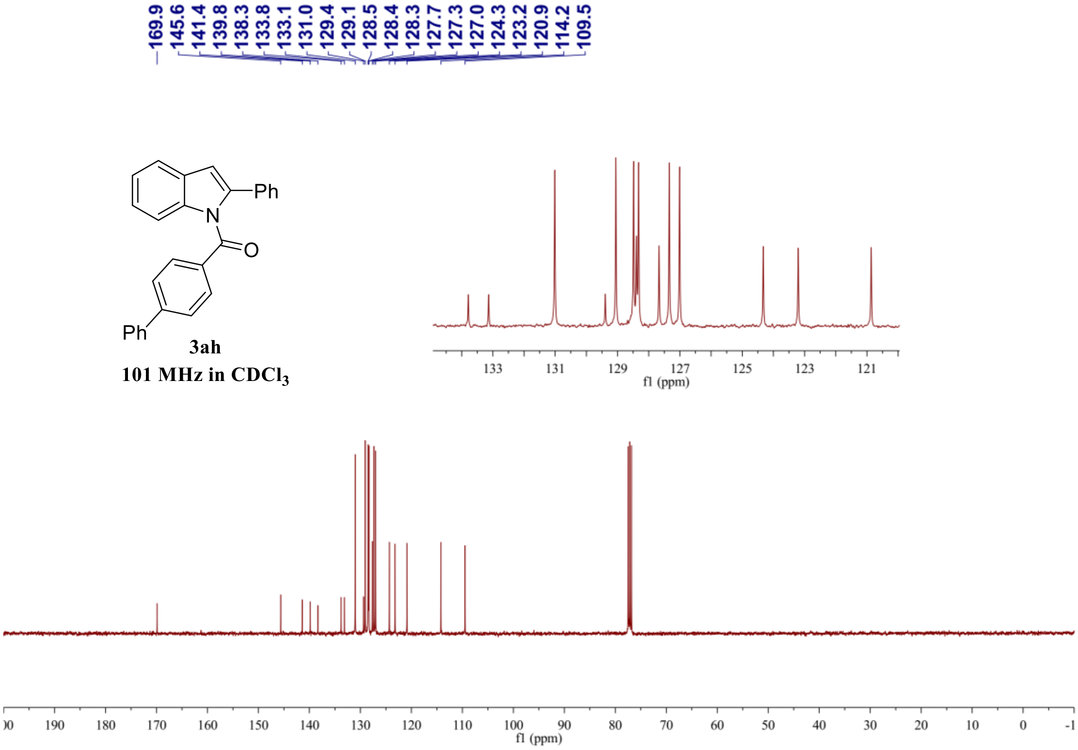

7.91 7.91 7.90 7.89 7.88 7.67 7.67 7.66 7.65 7.64 7.46 7.44 7.36 7.36 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.24 7.24 7.24 7.23 7.22 7.22 7.17 7.17 7.16 7.15 7.13 7.12 7.12 7.11 7.11 7.10 7.09 7.09 6.79 1.57 H2O
Ph
N
O
F_3C
3ag
400 MHz in $CDCl_3$
0.97 3.02 2.10 2.12 2.01 3.09
f1 (ppm)
0.97 3.02 2.10 2.12 2.01 3.09 0.96
f1 (ppm)

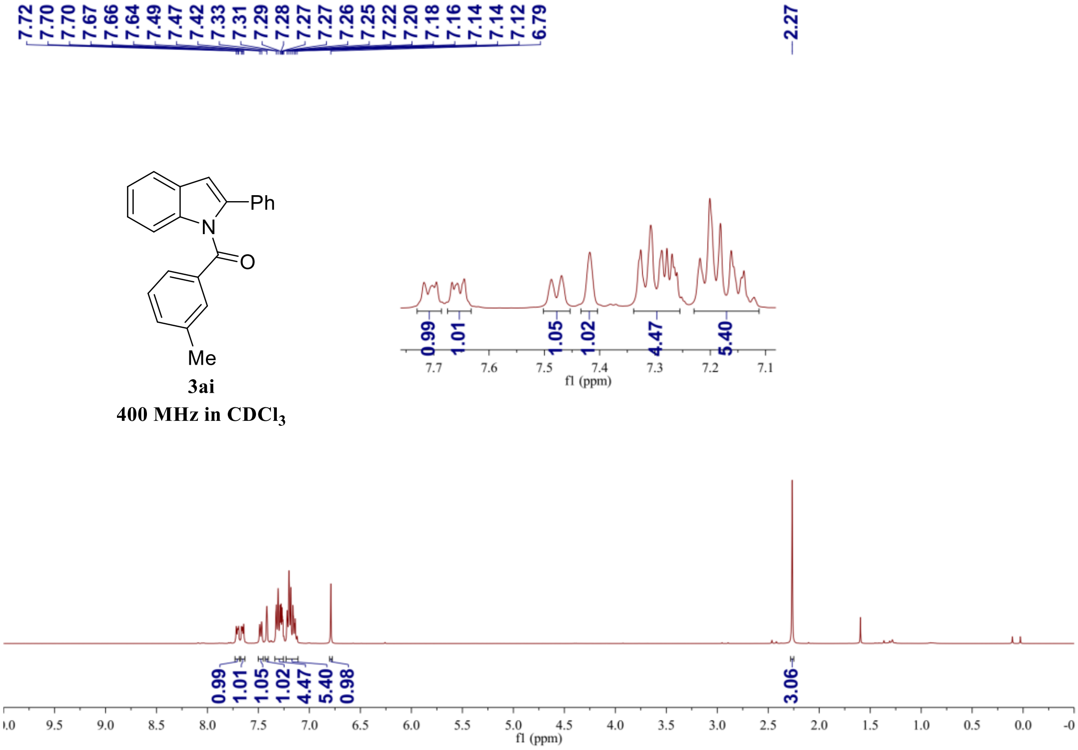

168.9 140.9 138.6 138.2 134.3 134.0 133.6 133.3 132.9 130.4 129.4 128.7 128.4 127.9 127.5 125.2 125.2 125.2 125.1 124.9 124.8 123.8 122.1 121.0 119.4 114.5 110.4
Ph
N
O
F_3C
3ag
101 MHz in $CDCl_3$
f1 (ppm)
f1 (ppm)

3ah
400 MHz in $CDCl_3$

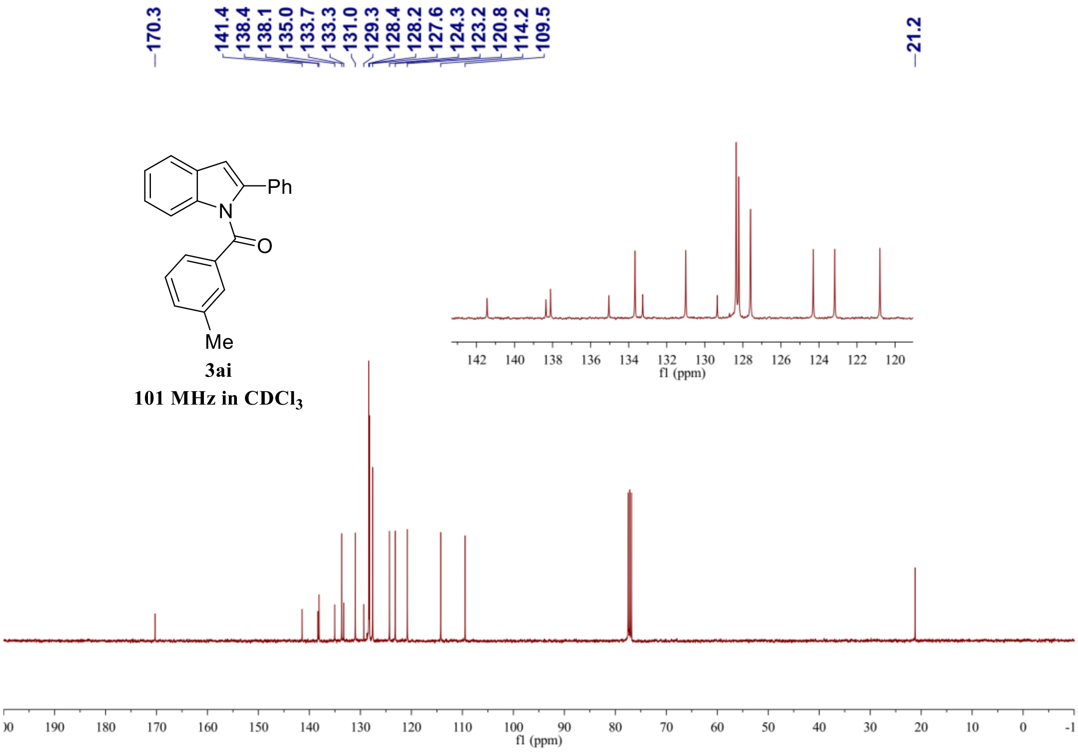


3ah
101 MHz in $CDCl_3$

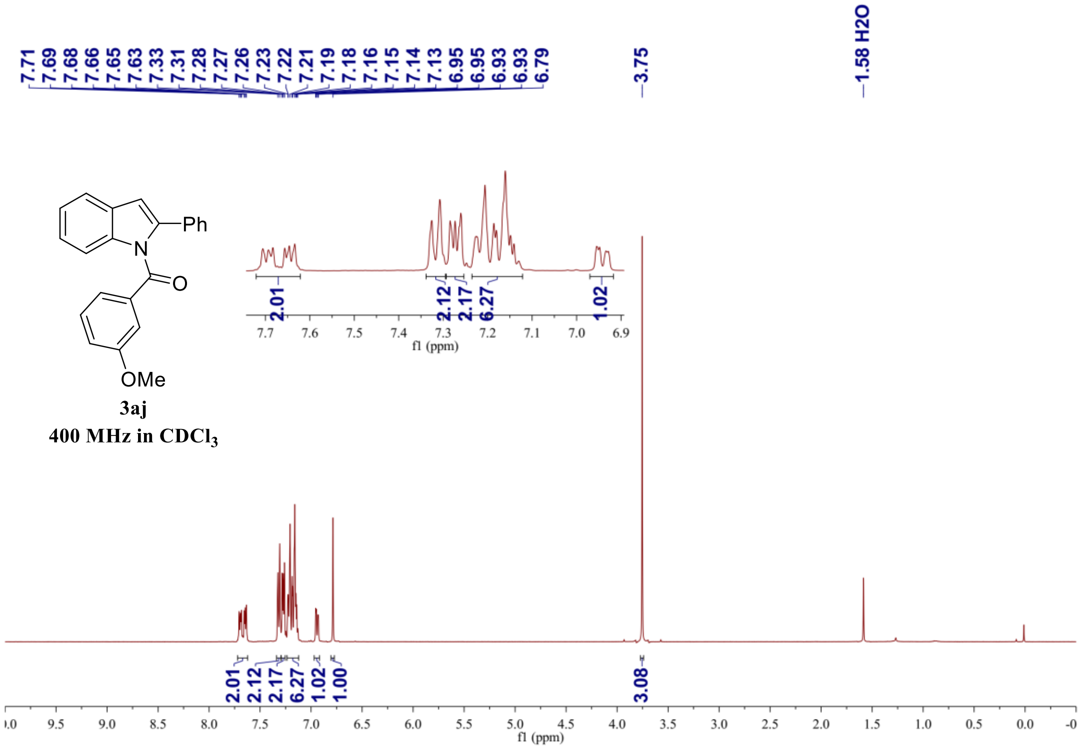


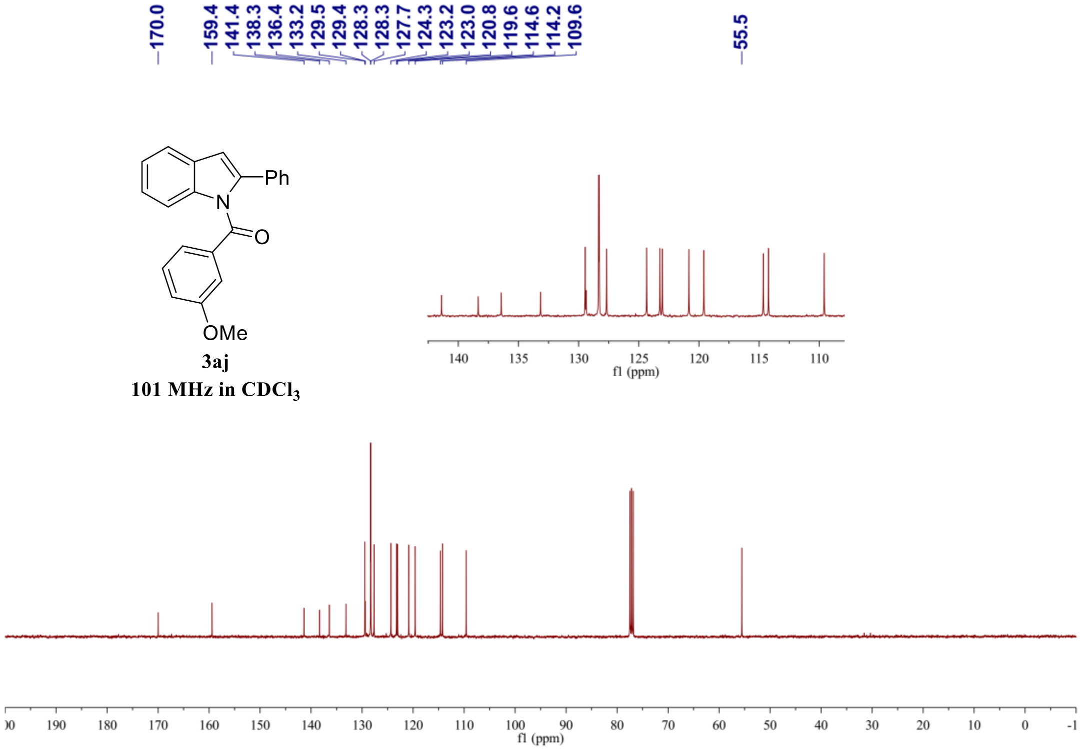


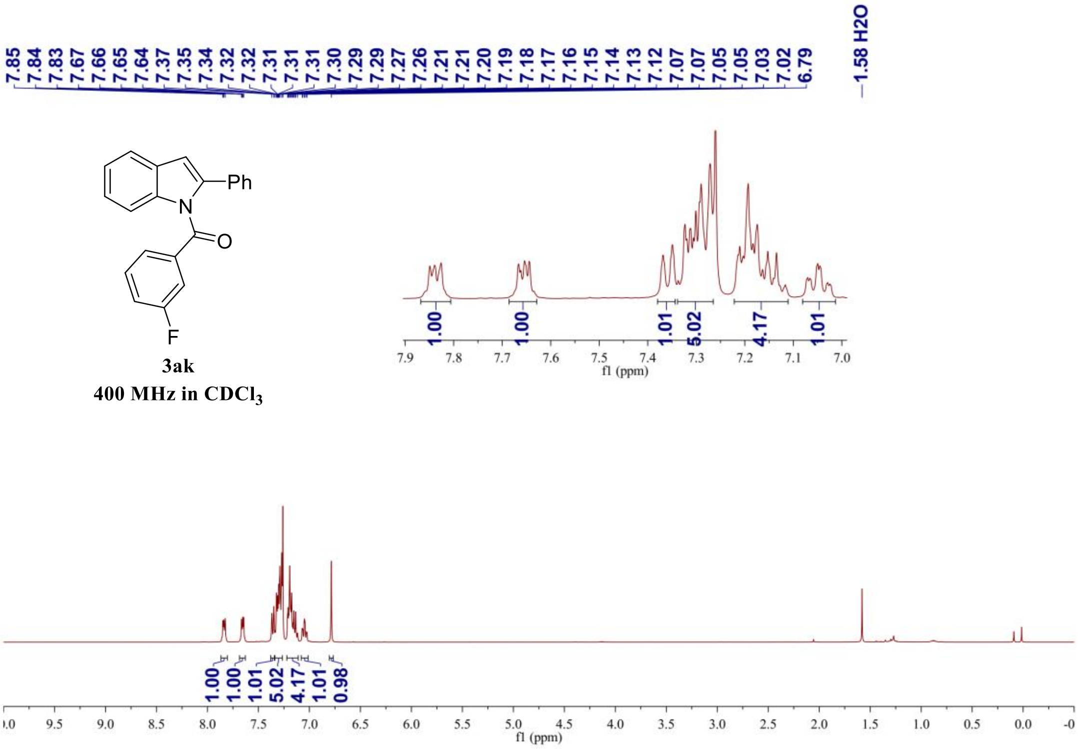
3ai
400 MHz in $CDCl_3$



3ai
101 MHz in $CDCl_3$

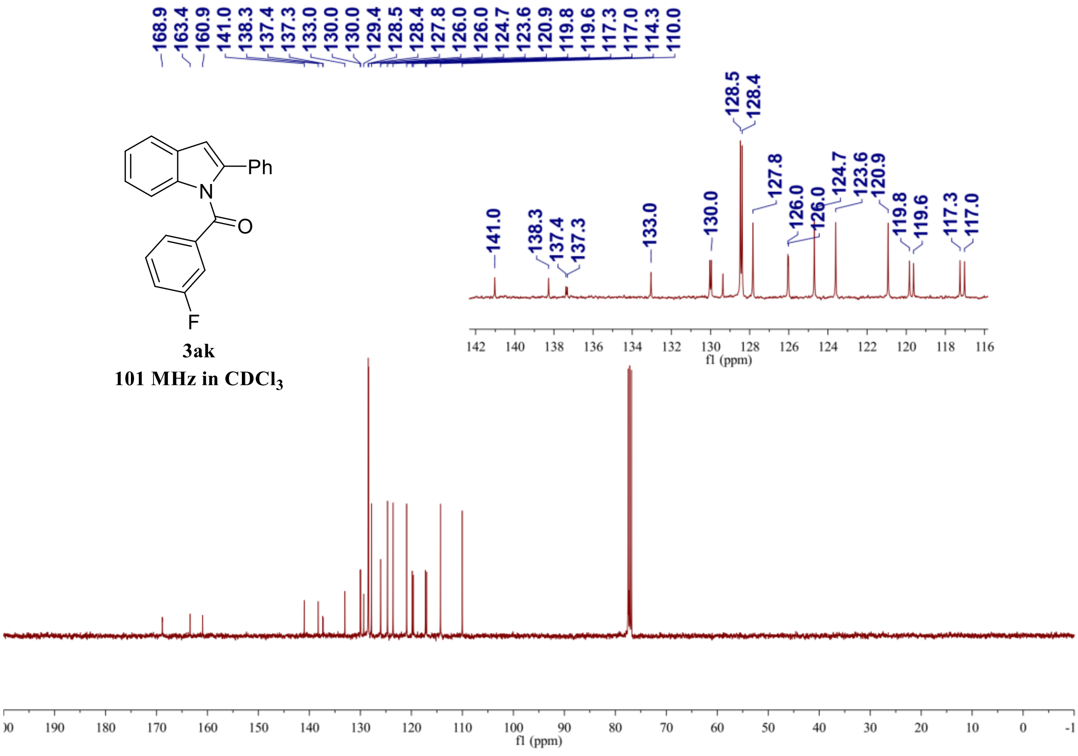

7.71 7.69 7.68 7.66 7.65 7.63 7.33 7.31 7.28 7.27 7.26 7.23 7.22 7.21 7.19 7.18 7.16 7.15 7.14 7.13 6.95 6.95 6.93 6.93 6.79
3.75
1.58 H2O
Ph
N
O
OMe
3aj
400 MHz in CDCl3
2.01 2.12 2.17 6.27 1.02
2.01 2.12 2.17 6.27 1.02 1.00
3.08
f1 (ppm)


170.0
159.4 141.4 138.3 136.4 133.2 129.5 129.4 128.3 128.3 127.7 124.3 123.2 123.0 120.8 119.6 114.6 114.2 109.6
55.5
Ph
N
O
OMe
3aj
101 MHz in CDCl3
f1 (ppm)



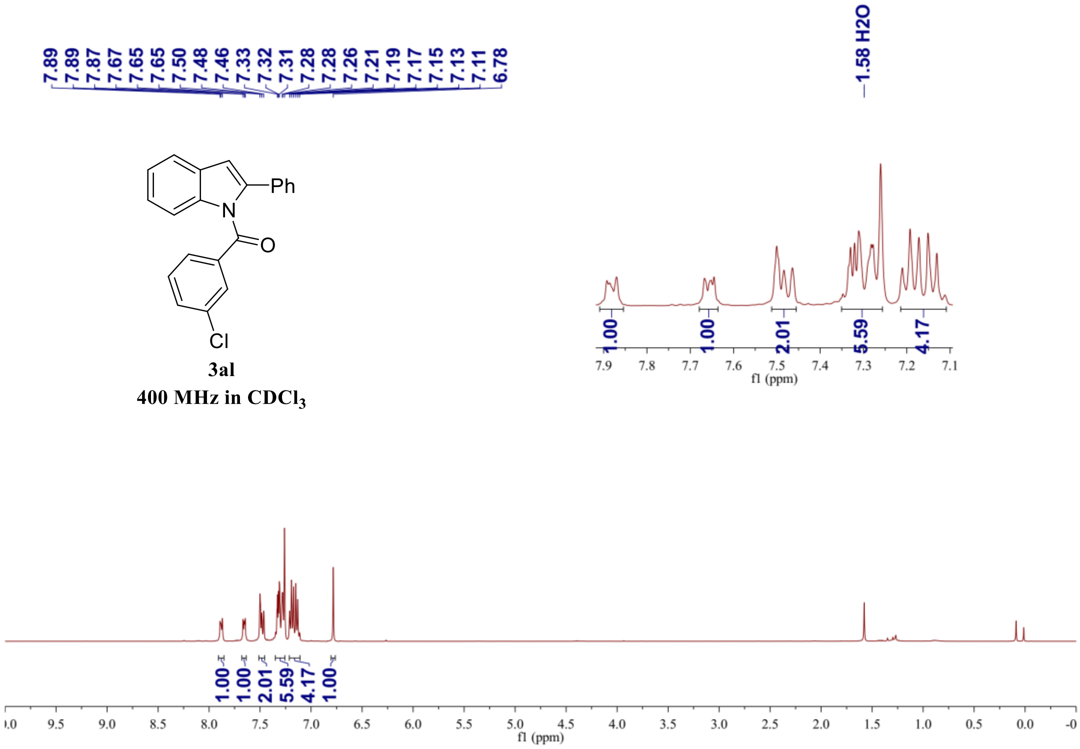
3ak

400 MHz in $CDCl_3$



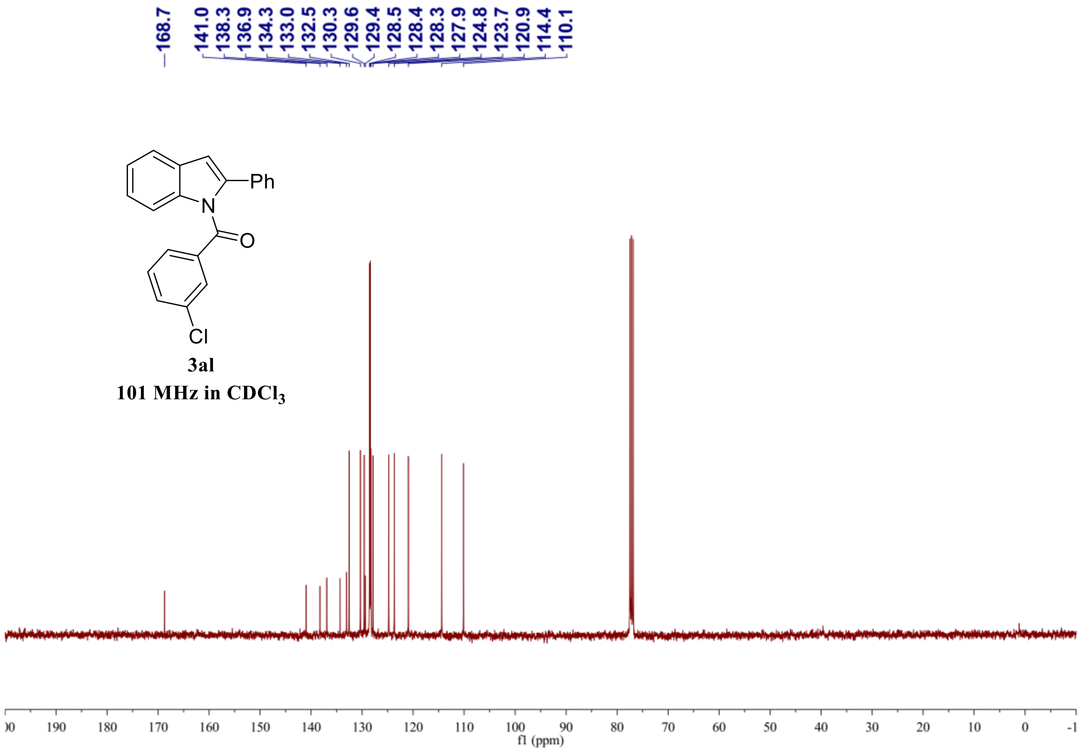
3ak

101 MHz in $CDCl_3$



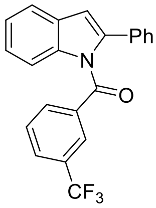
3al

400 MHz in $CDCl_3$



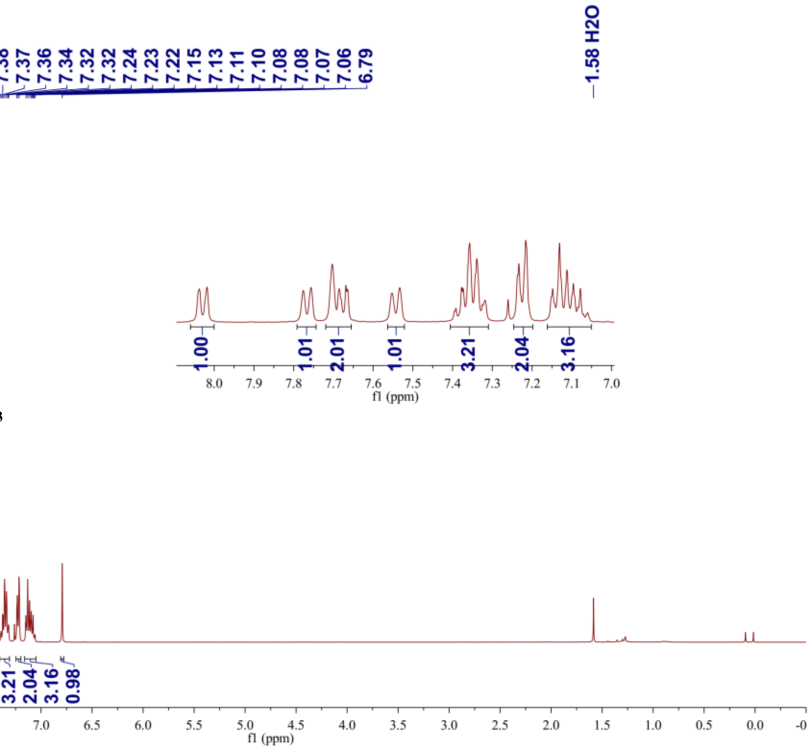
3al

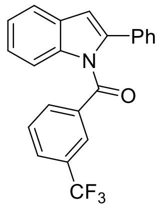
101 MHz in $CDCl_3$



3am

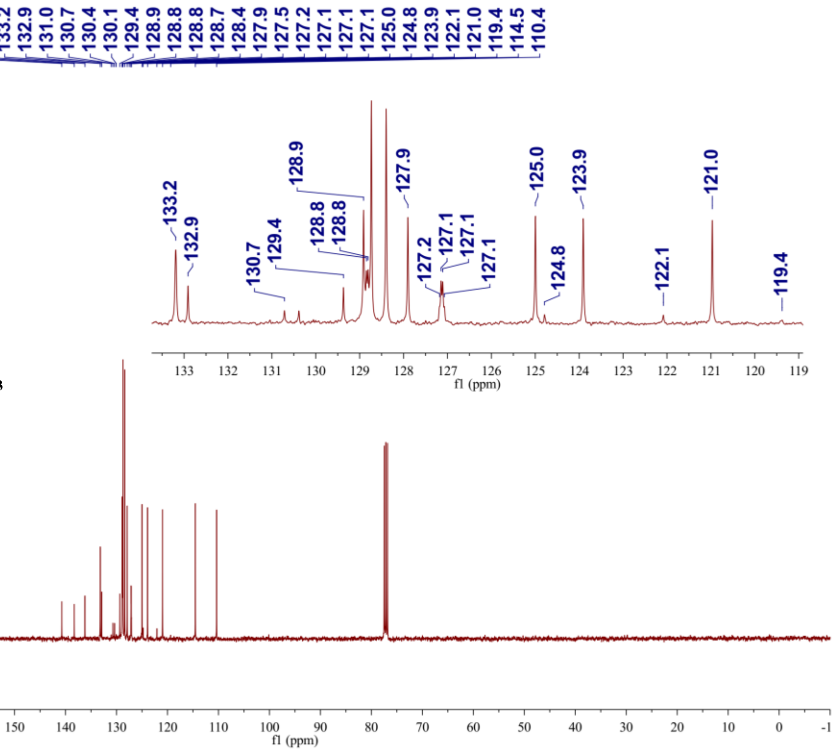
400 MHz in $CDCl_3$

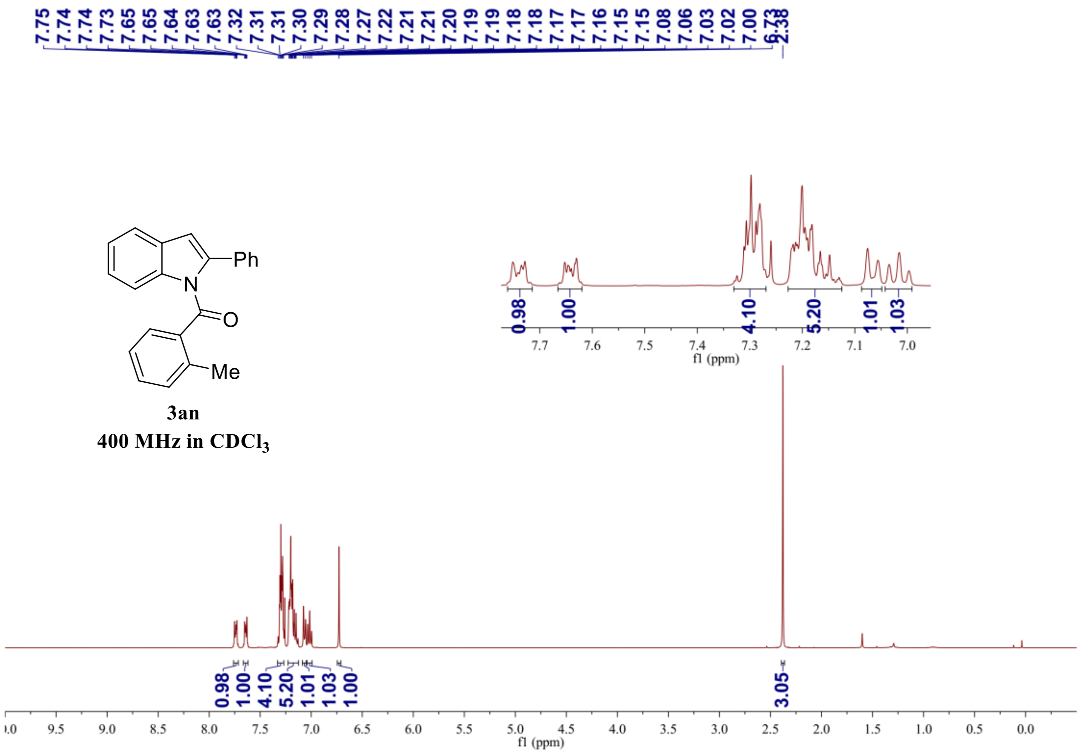




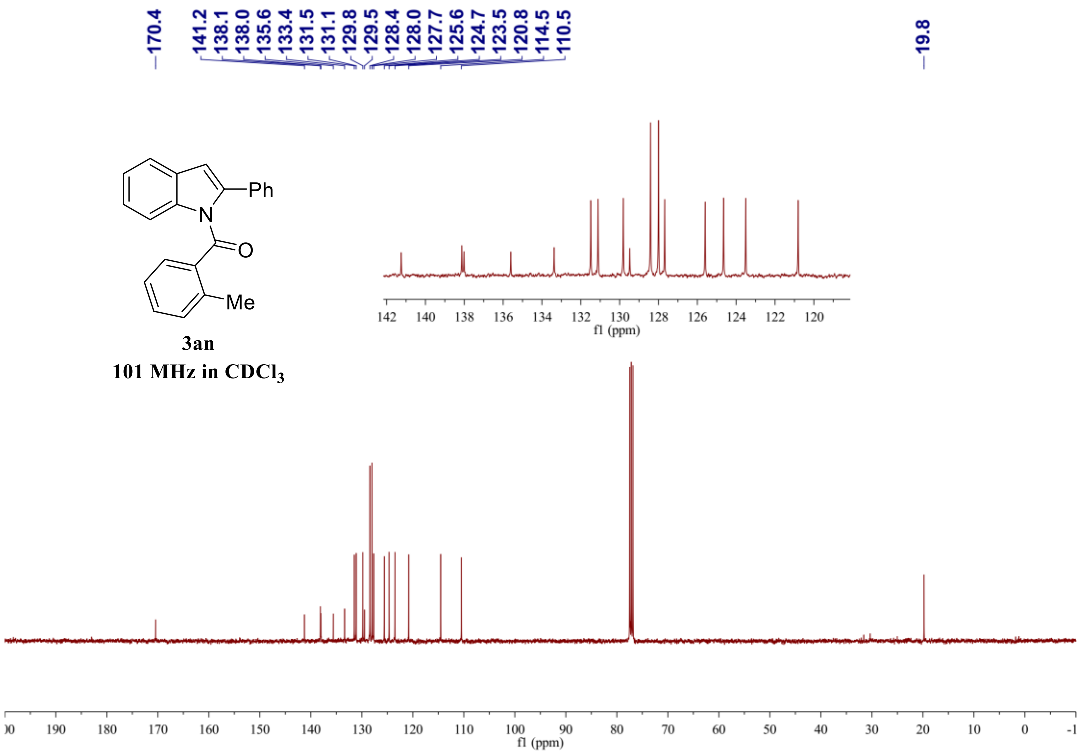
3am

101 MHz in $CDCl_3$

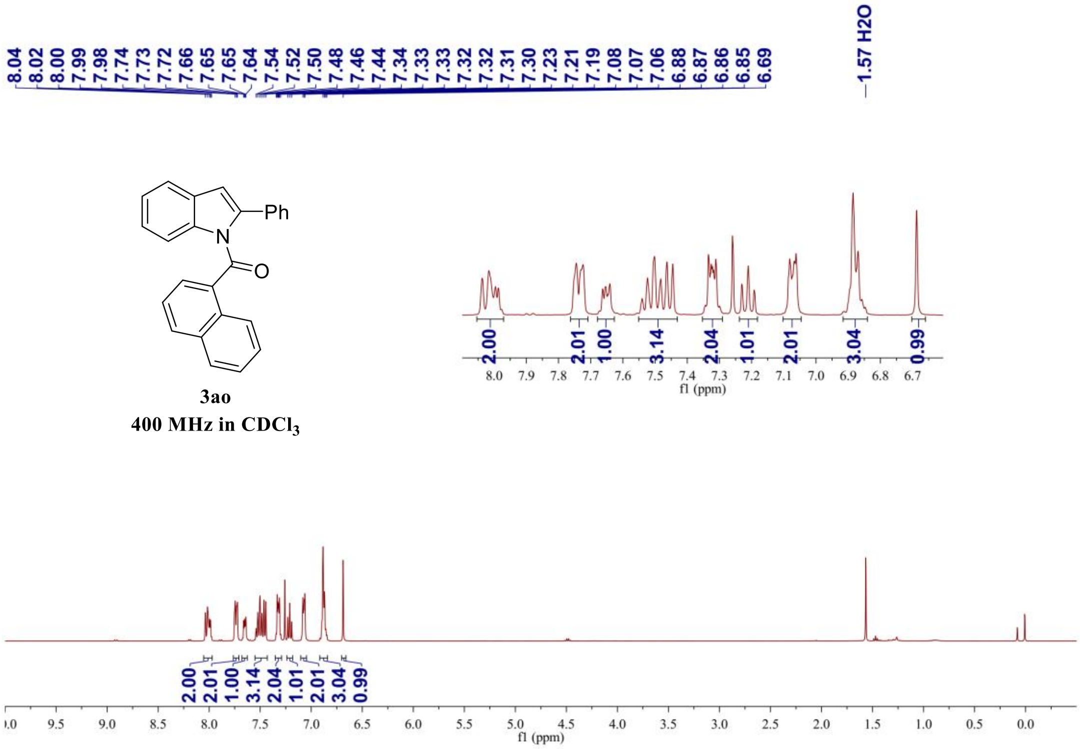




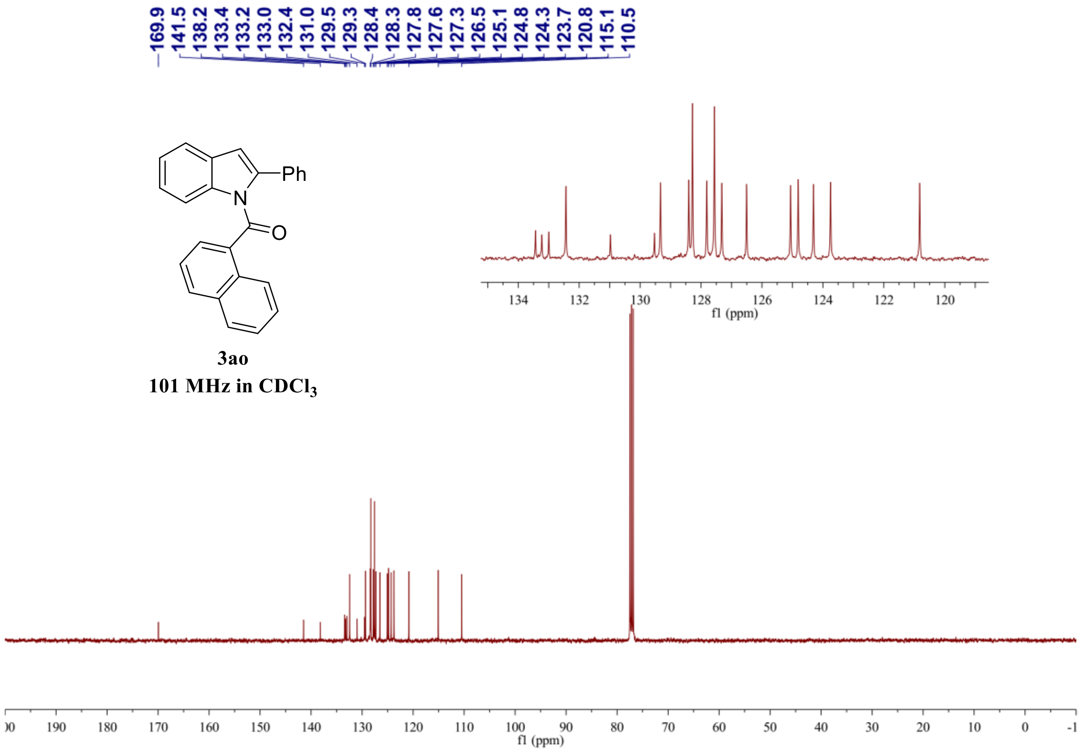
3an
400 MHz in $CDCl_3$



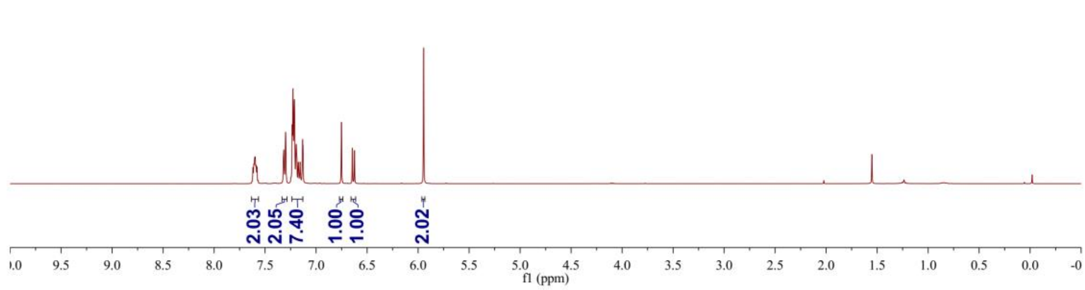
3an
101 MHz in $CDCl_3$

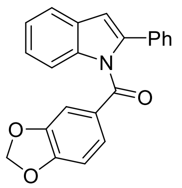


3ao
400 MHz in $CDCl_3$

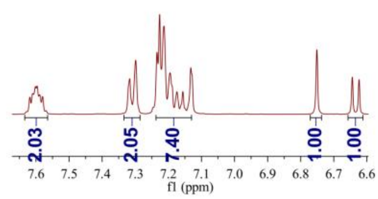


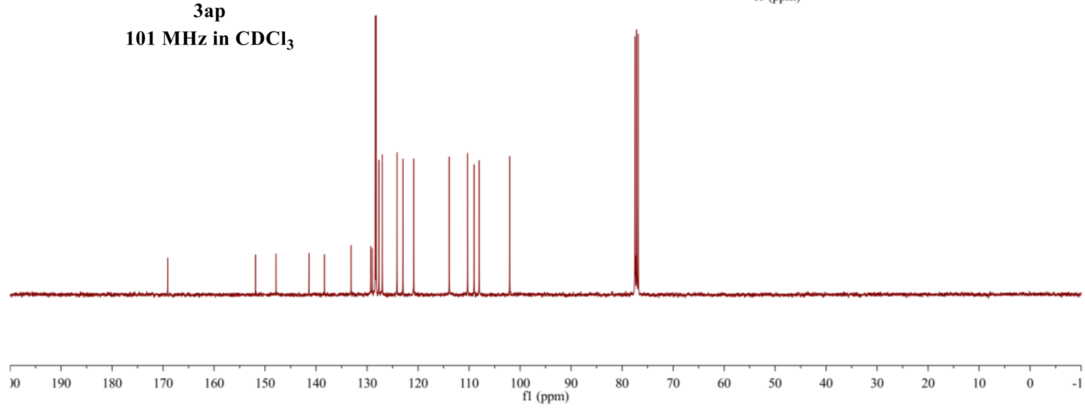
3ao
101 MHz in $CDCl_3$

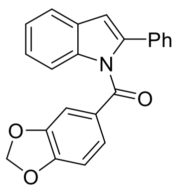




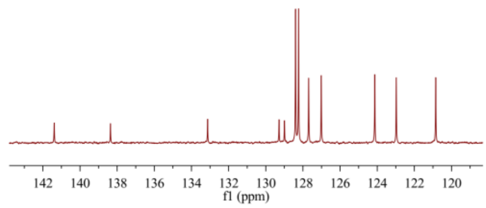
3ap
400 MHz in $CDCl_3$

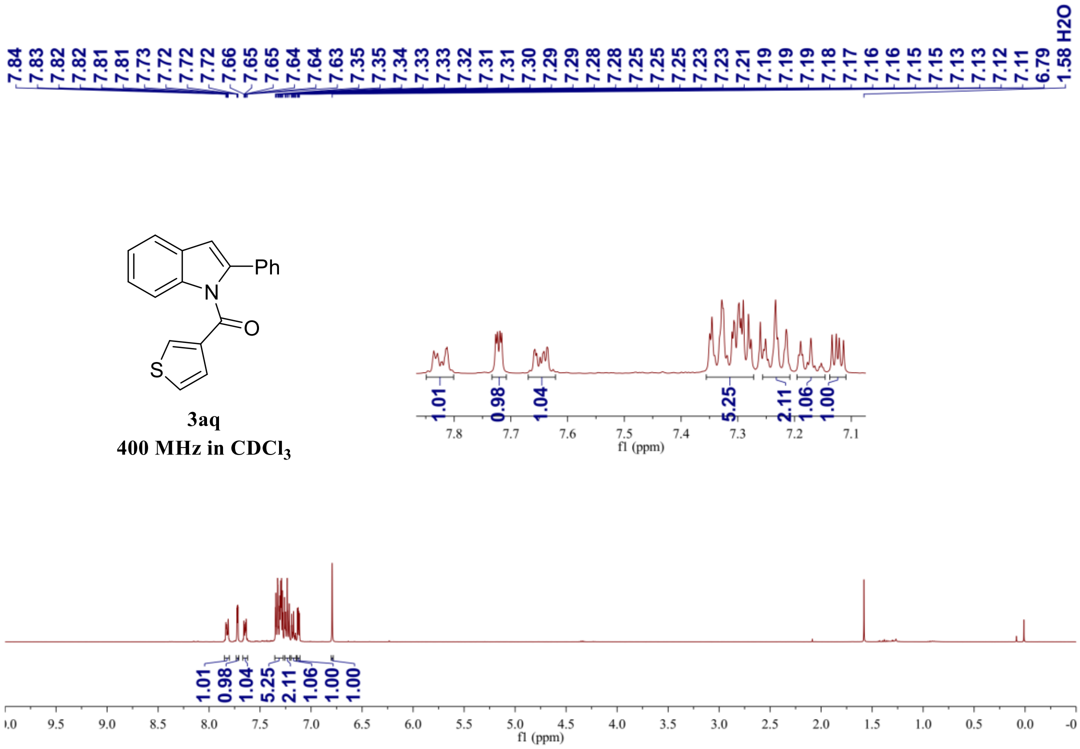




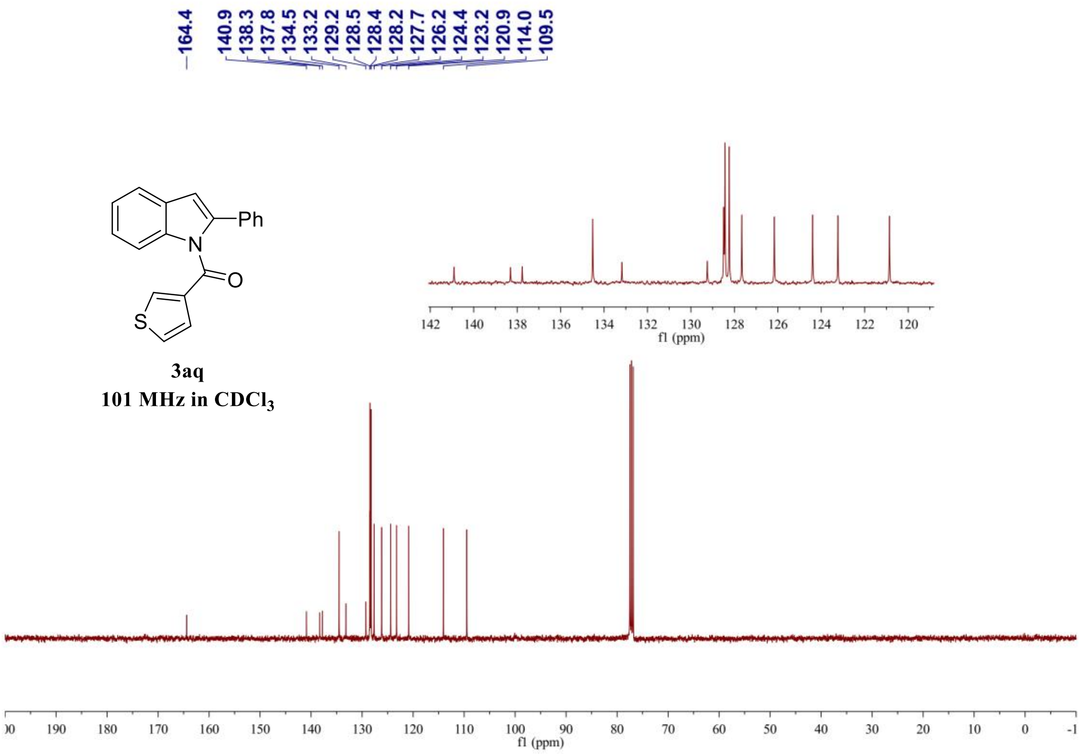


3ap
101 MHz in $CDCl_3$

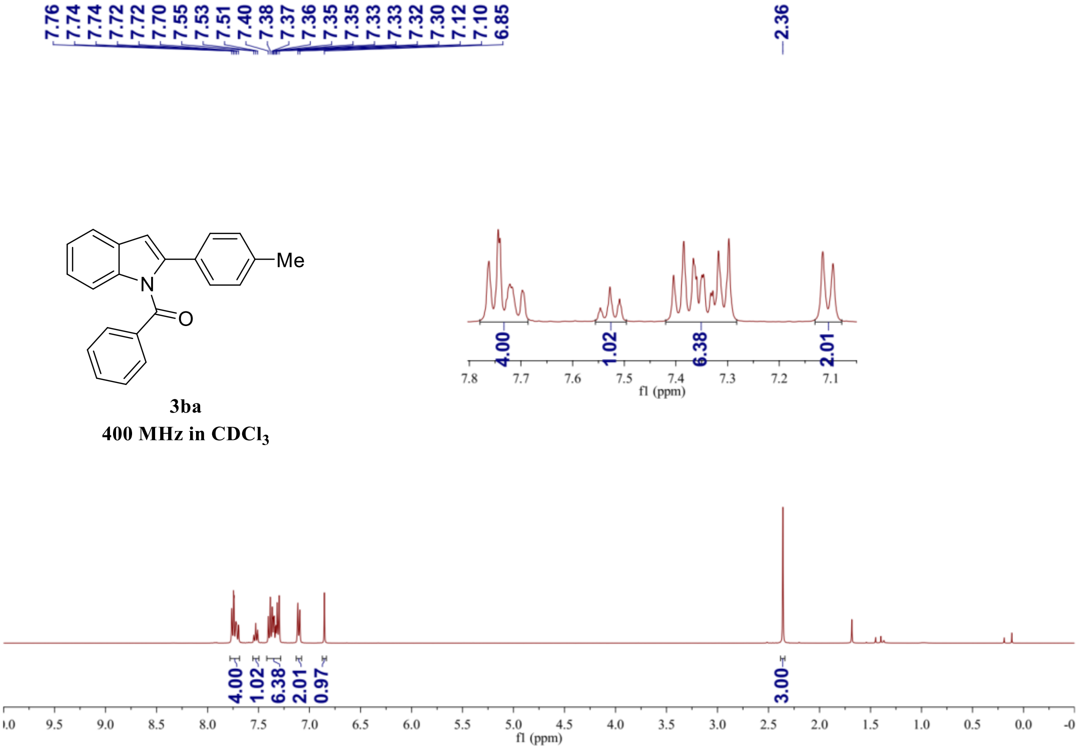




3aq
400 MHz in $CDCl_3$

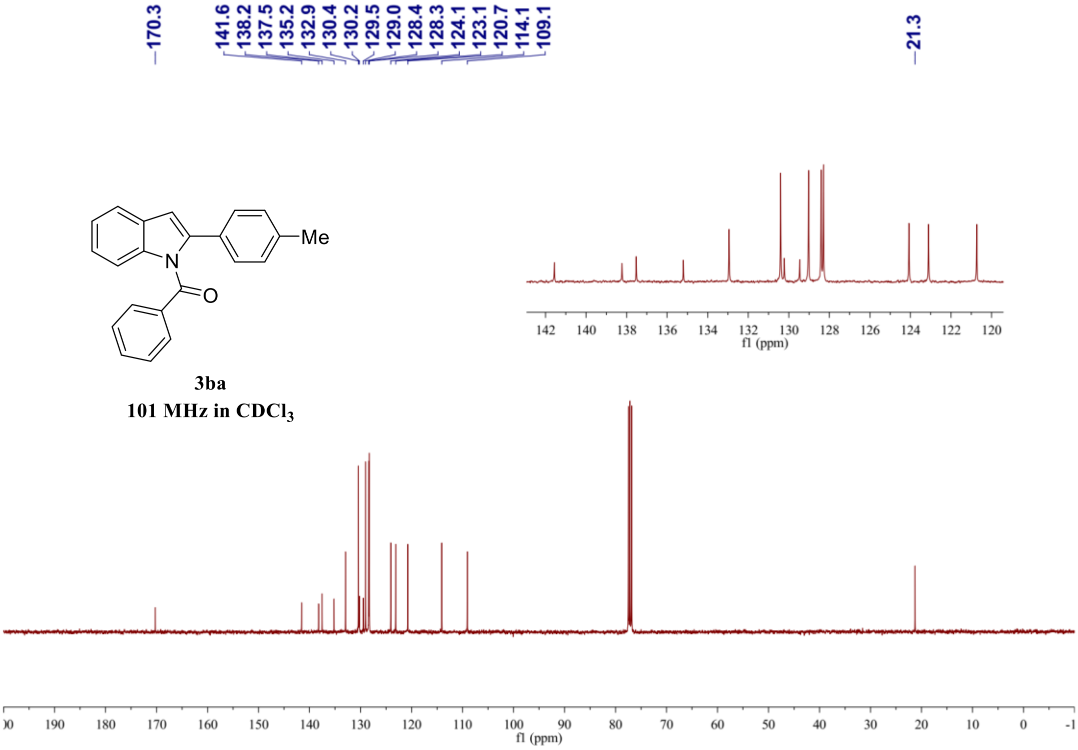


3aq
101 MHz in $CDCl_3$



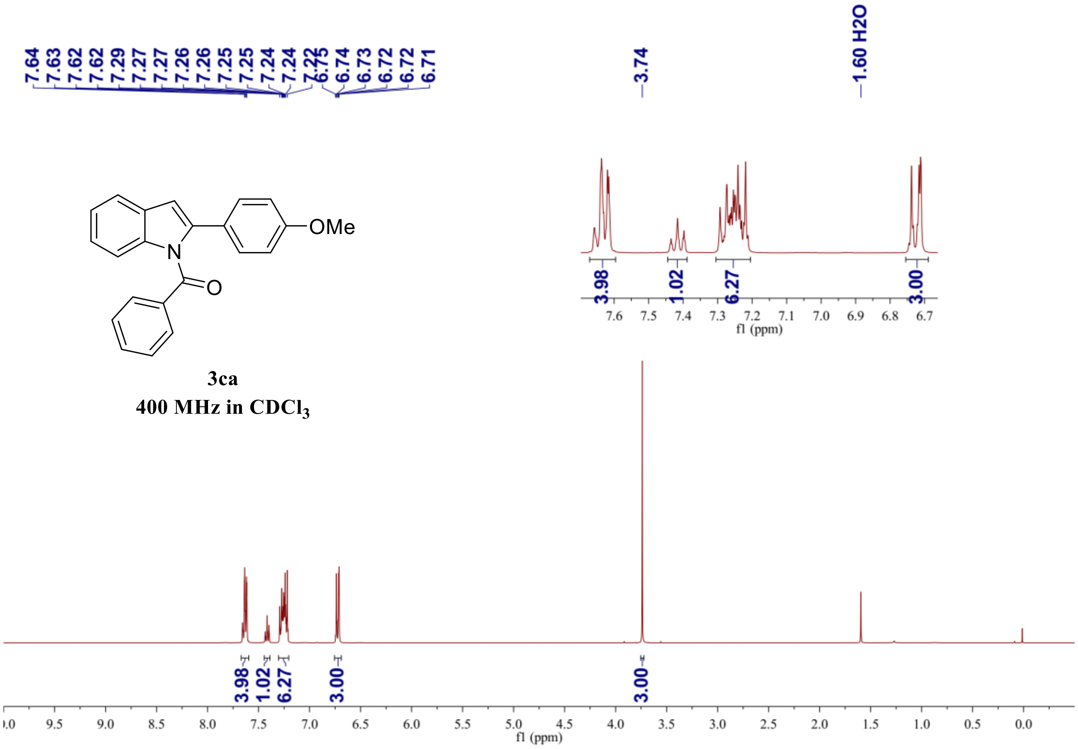
3ba

400 MHz in $CDCl_3$

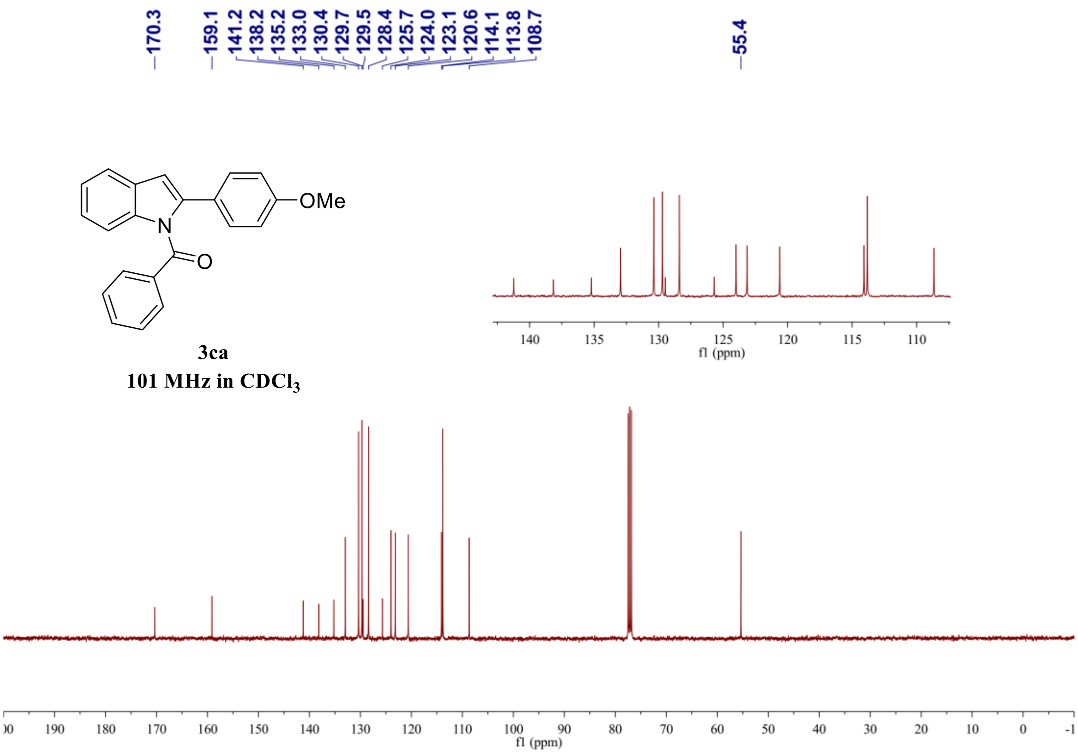


3ba

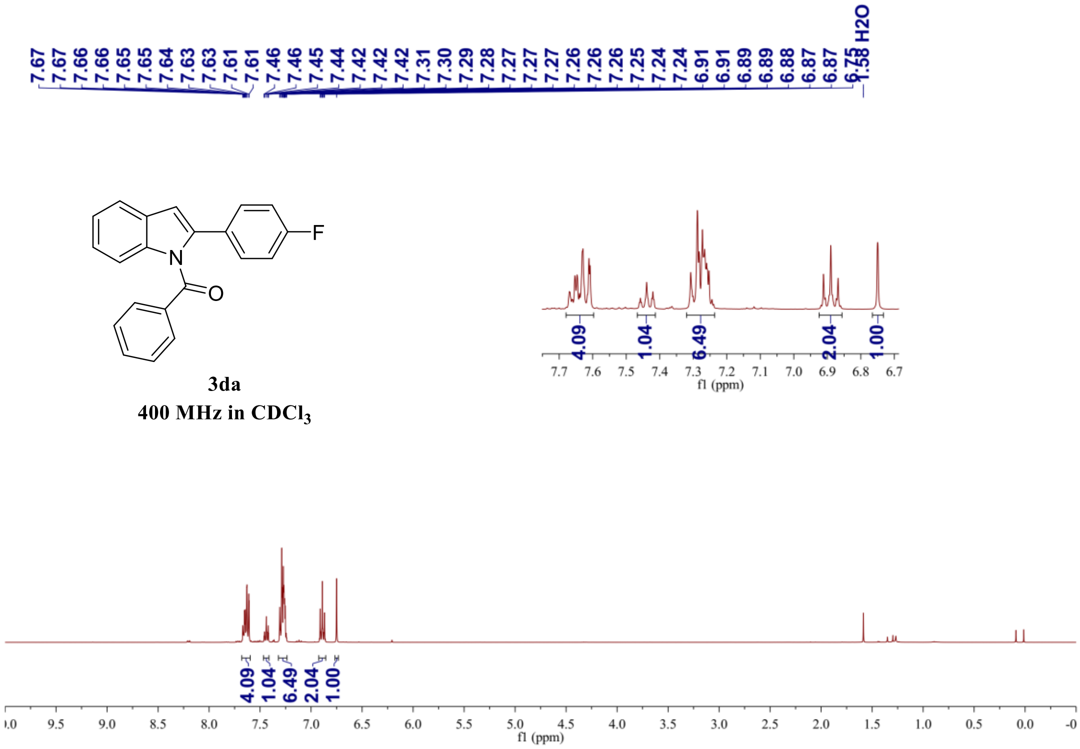
101 MHz in $CDCl_3$



3ca
400 MHz in $CDCl_3$

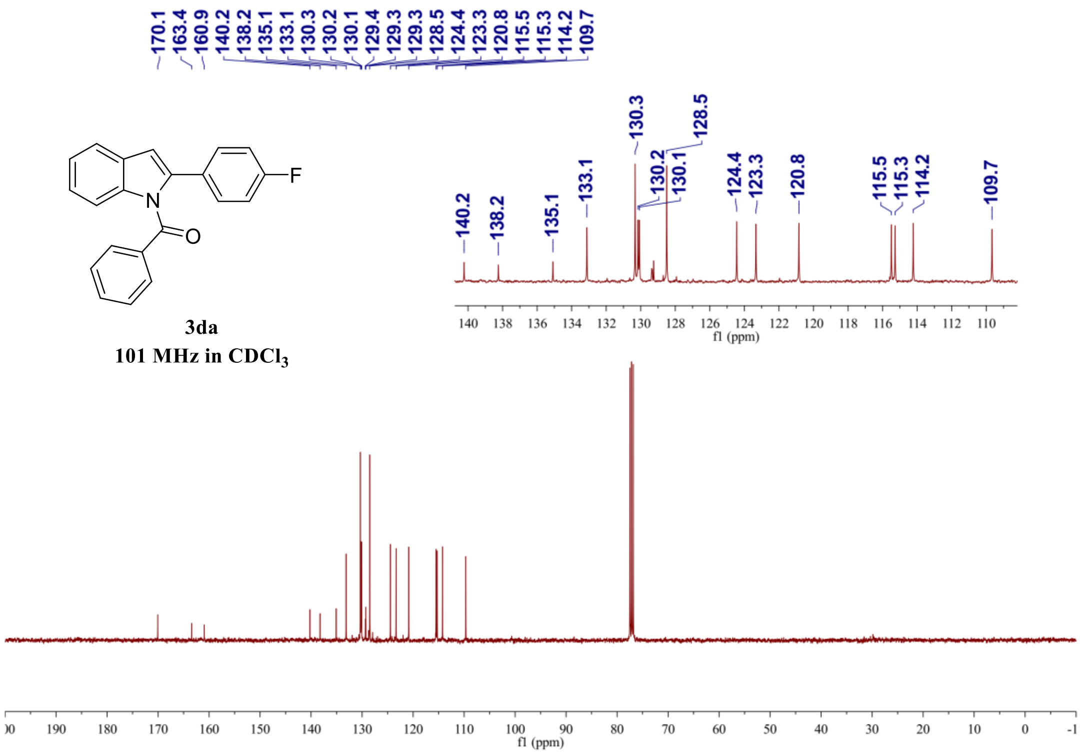


3ca
101 MHz in $CDCl_3$



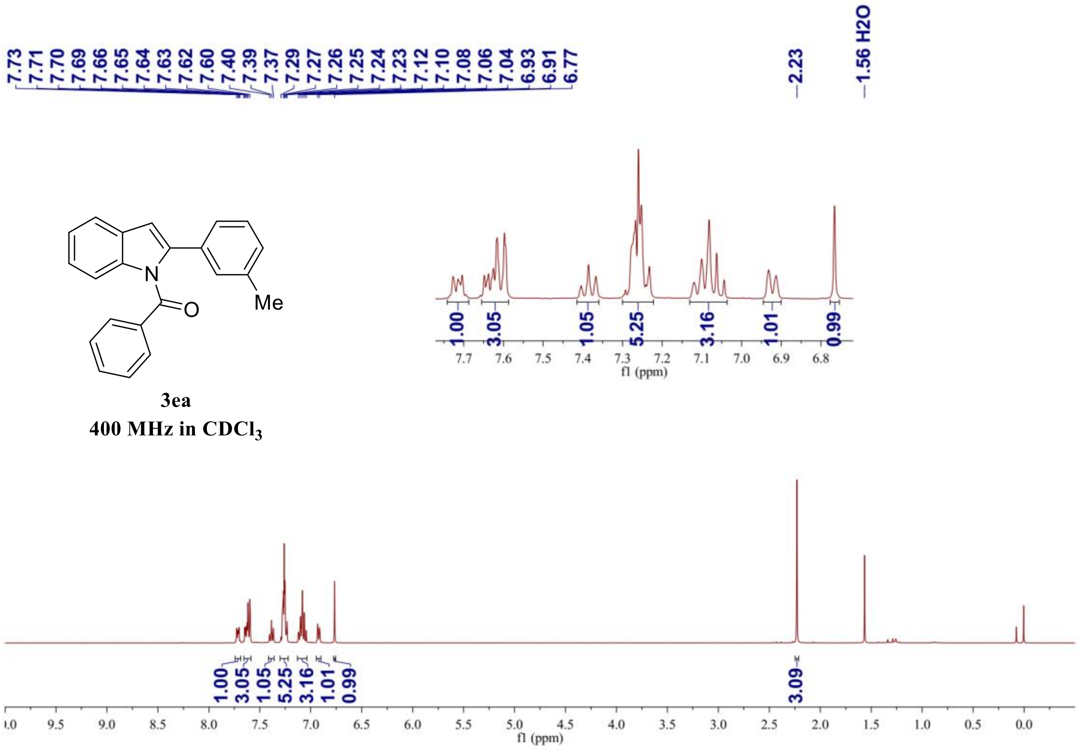
3da

400 MHz in $CDCl_3$

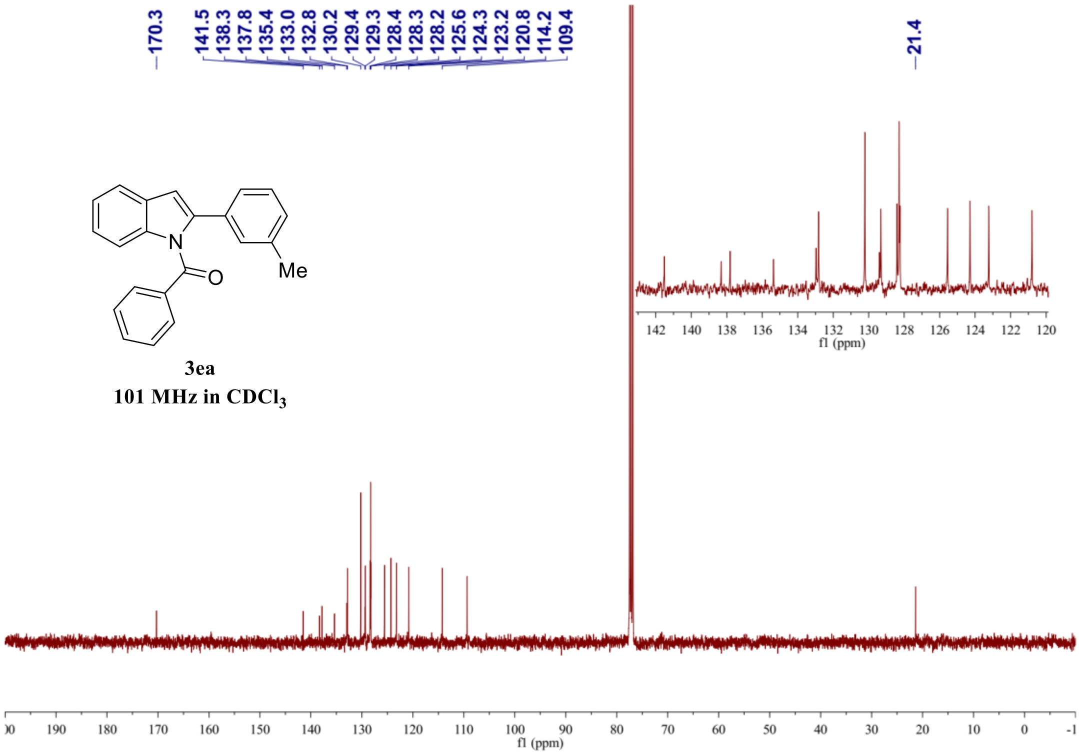


3da

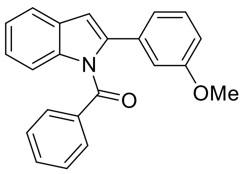
101 MHz in $CDCl_3$

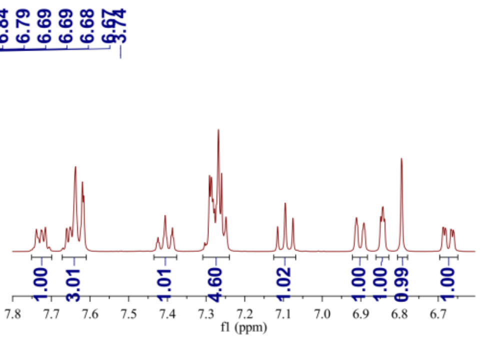


3ea
400 MHz in $CDCl_3$



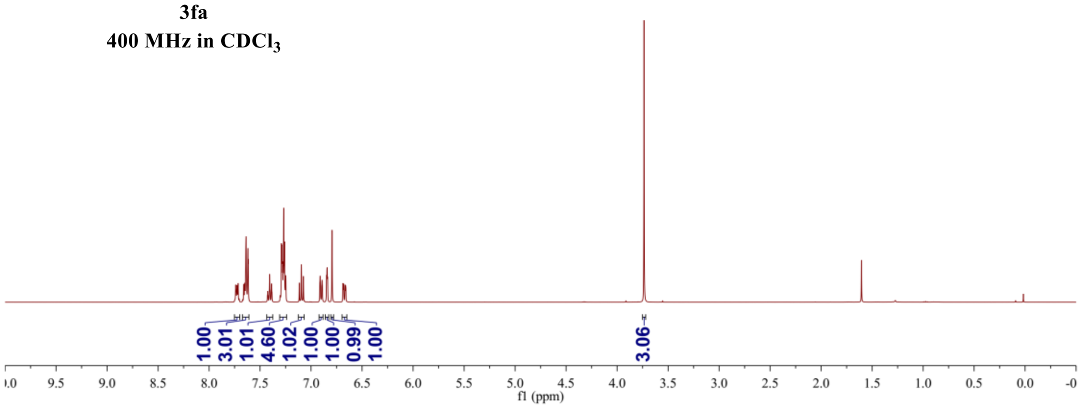
3ea
101 MHz in $CDCl_3$

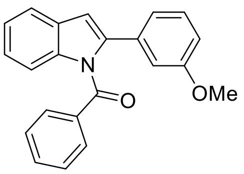


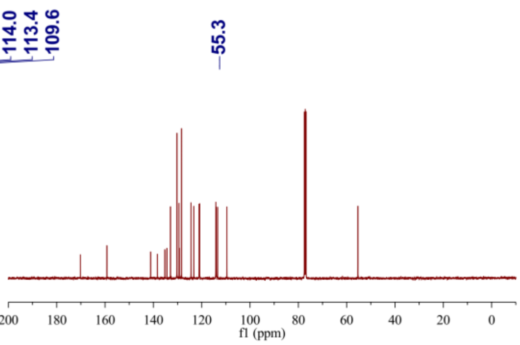


3fa

400 MHz in $CDCl_3$

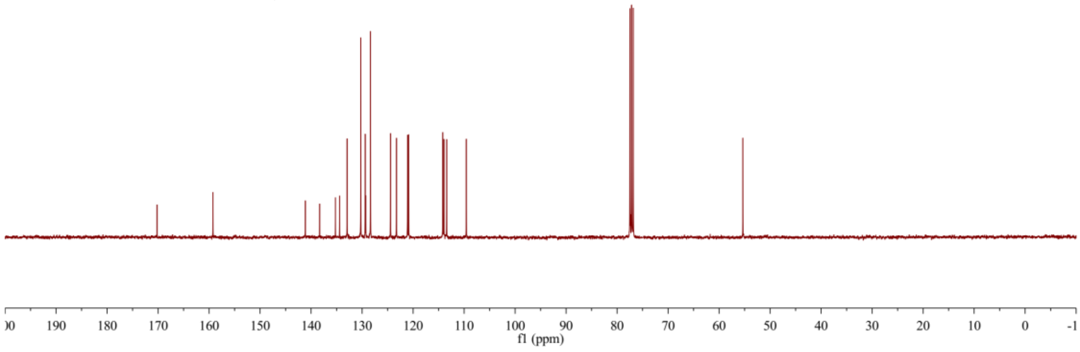


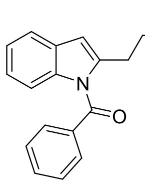




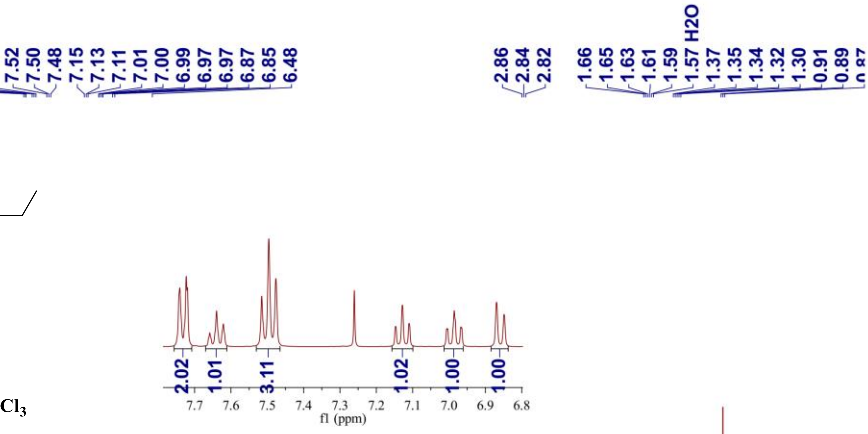
3fa

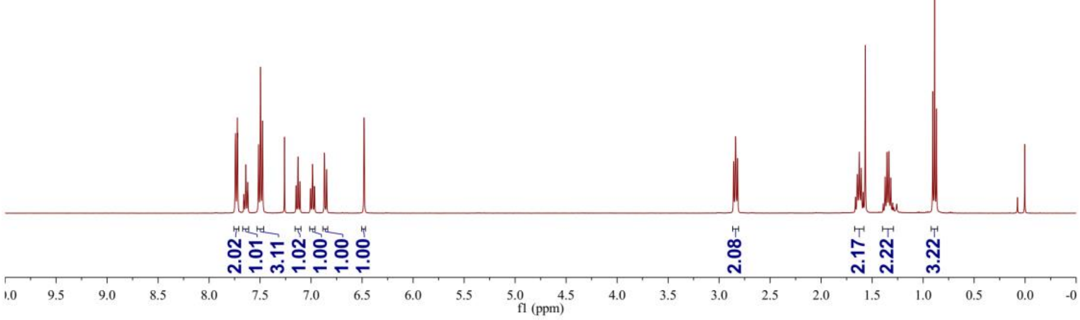
101 MHz in $CDCl_3$

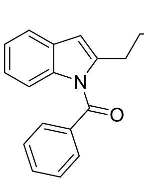




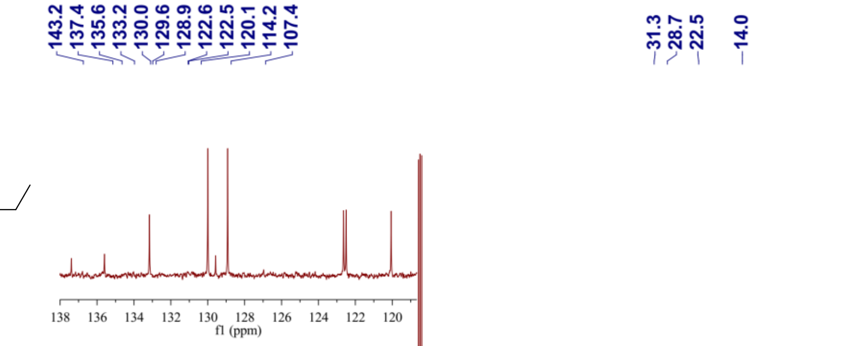
3ga
400 MHz in $CDCl_3$

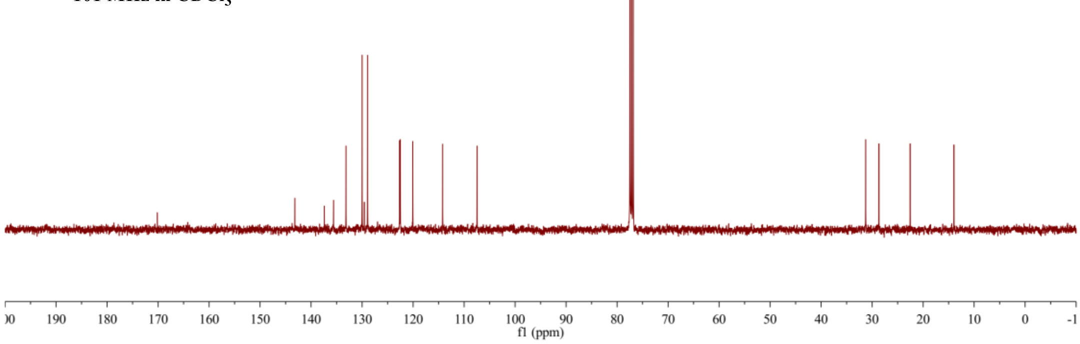


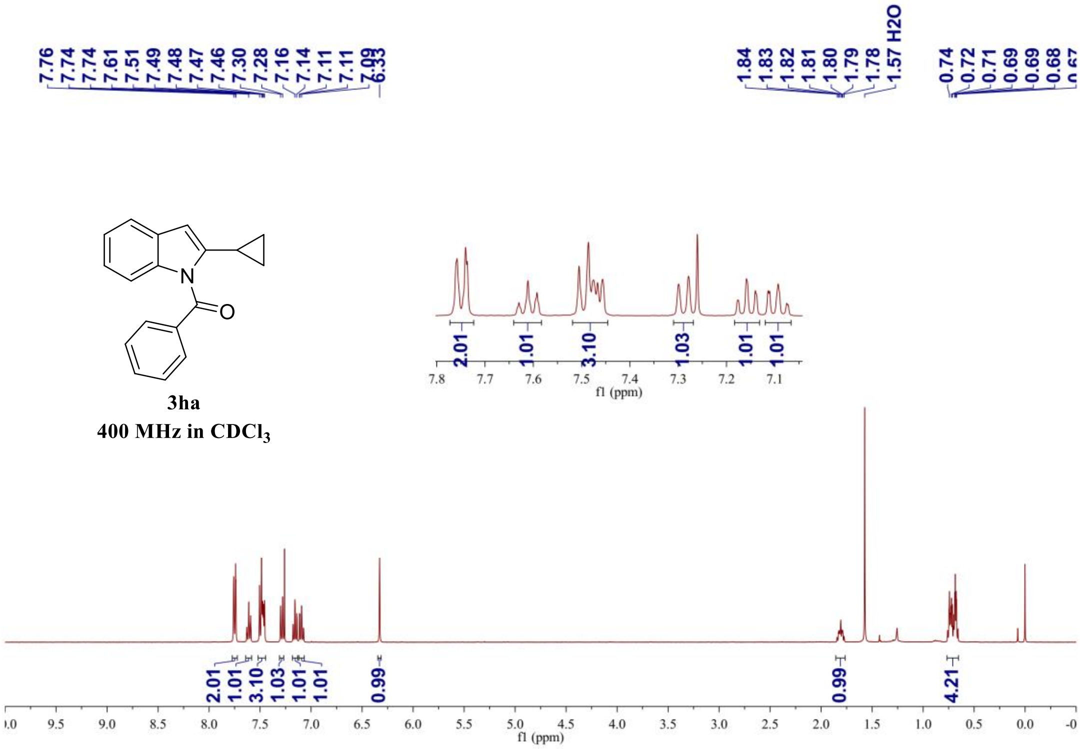




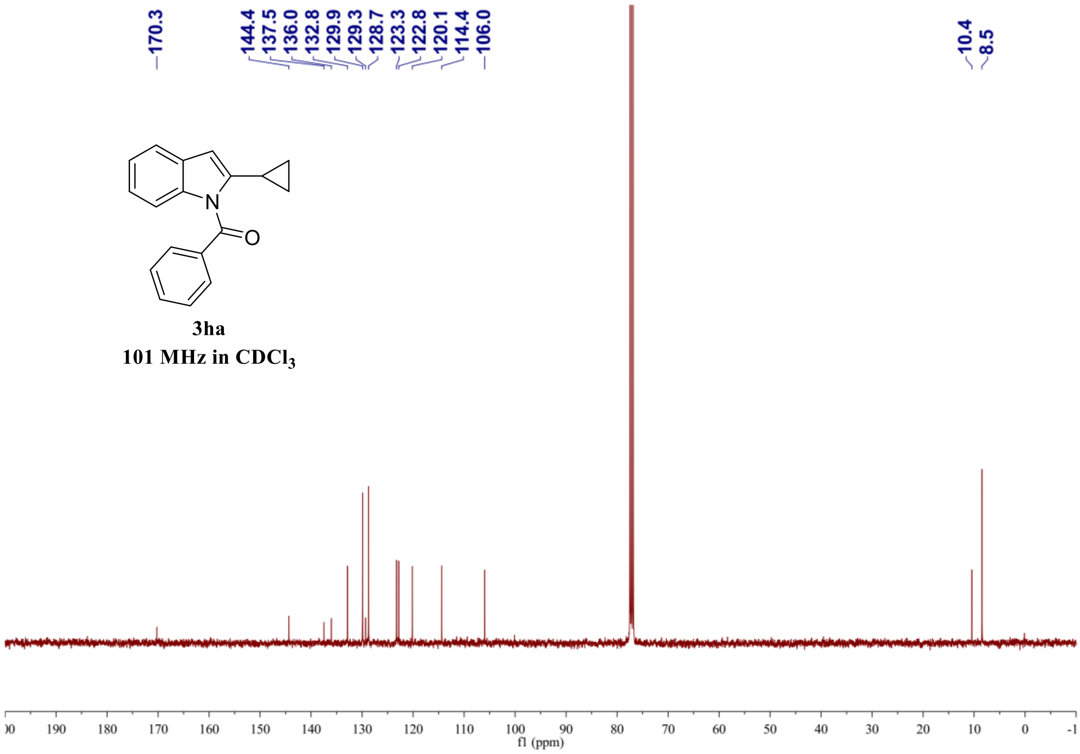
3ga
101 MHz in $CDCl_3$



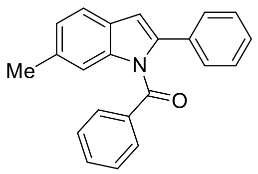




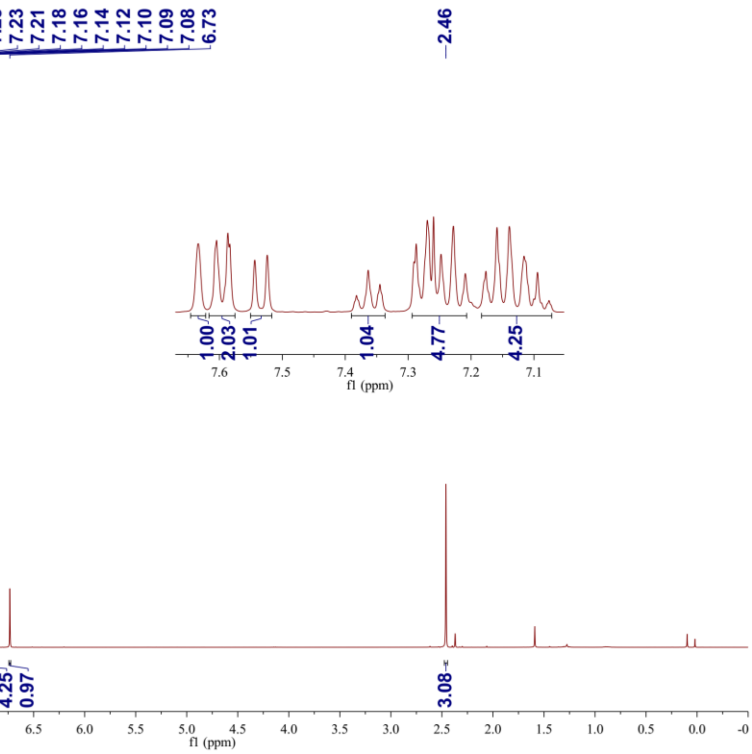
3ha
400 MHz in CDCl$_3$

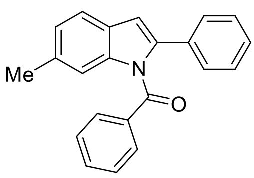


3ha
101 MHz in CDCl$_3$

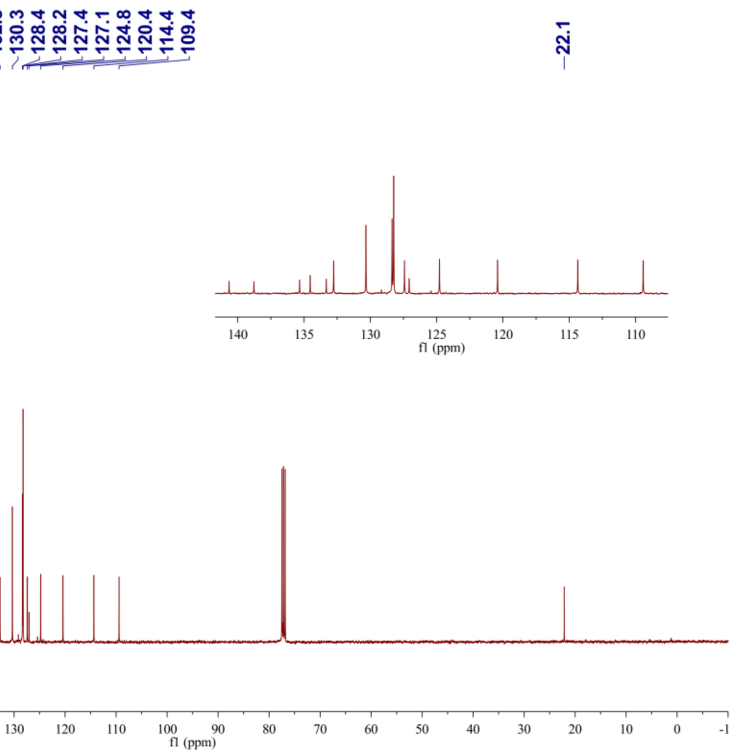


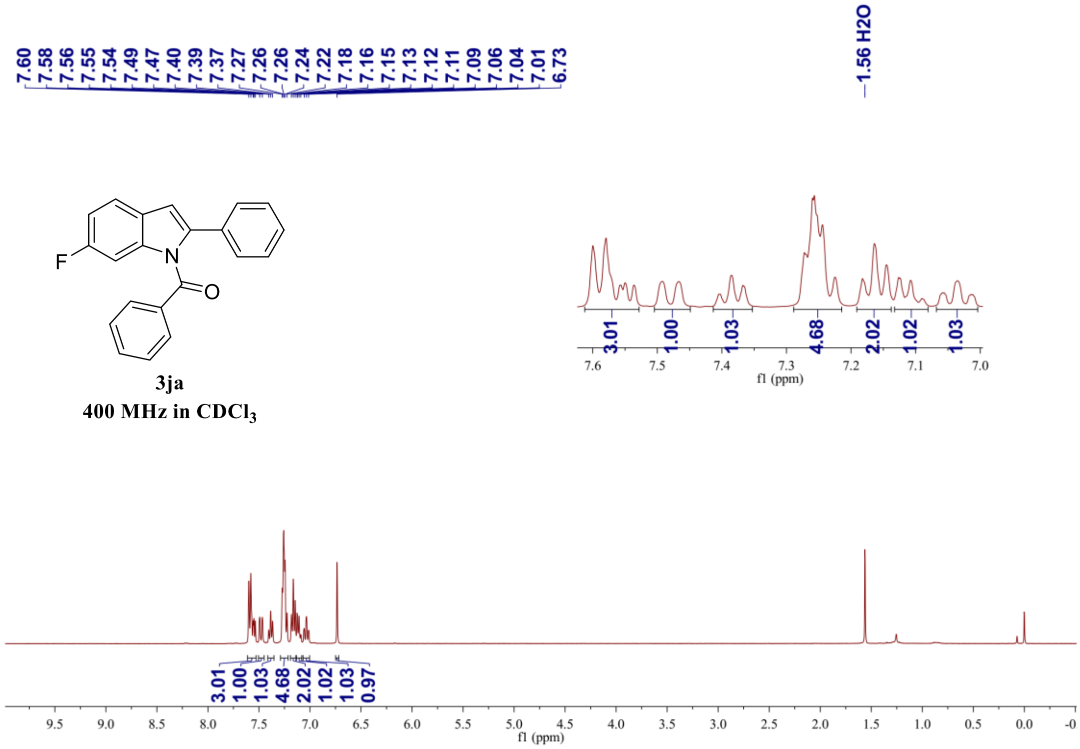
3ia
400 MHz in $CDCl_3$

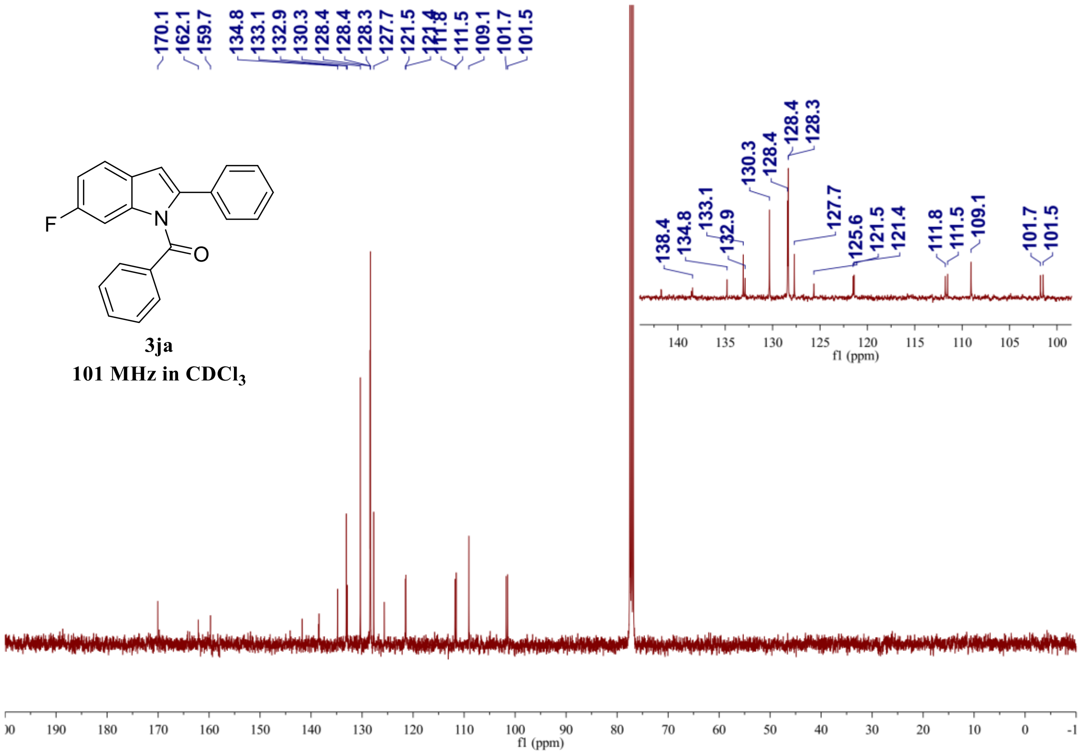


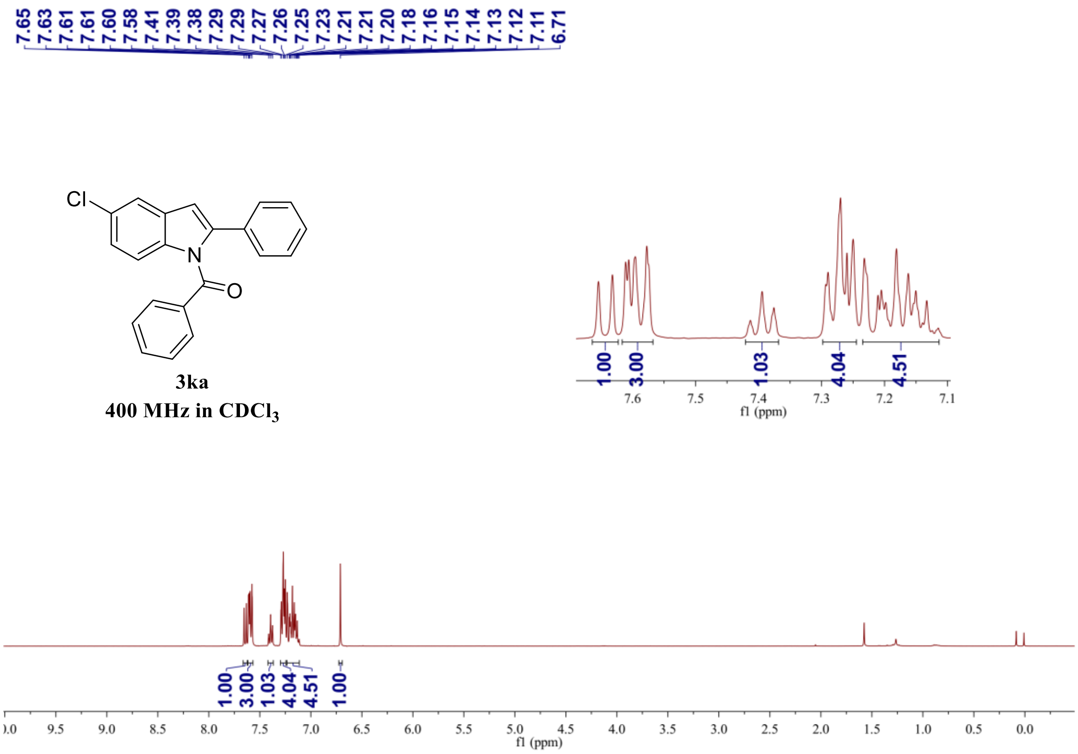


3ia
101 MHz in $CDCl_3$



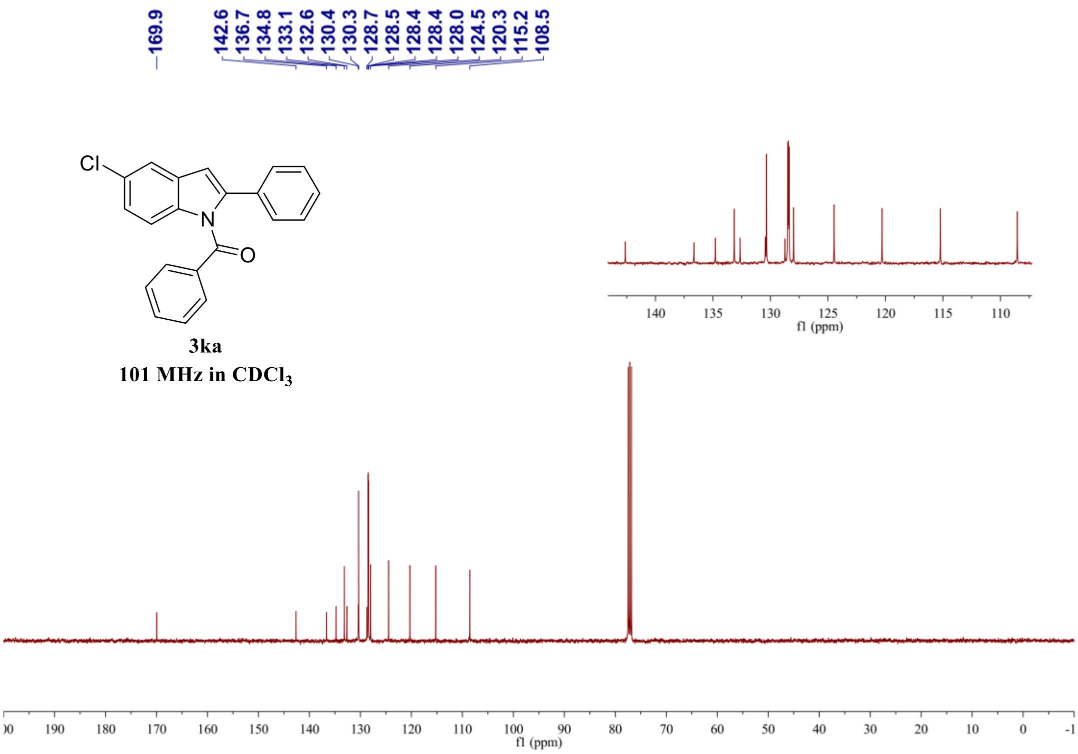

7.60 7.58 7.56 7.55 7.54 7.49 7.47 7.40 7.39 7.37 7.27 7.26 7.26 7.24 7.22 7.18 7.16 7.15 7.13 7.12 7.11 7.09 7.06 7.04 7.01 6.73
1.56 H2O
F
N
O
3ja
400 MHz in CDCl3
3.01 1.00 1.03 4.68 2.02 1.02 1.03
3.01 1.00 1.03 4.68 2.02 1.02 1.03 0.97
f1 (ppm)


170.1 162.1 159.7 134.8 133.1 132.9 130.3 128.4 128.4 128.3 127.7 121.5 121.4 111.8 111.5 109.1 101.7 101.5
F
N
O
3ja
101 MHz in CDCl3
138.4 134.8 133.1 132.9 130.3 128.4 128.4 128.3 127.7 125.6 121.5 121.4 111.8 111.5 109.1 101.7 101.5
f1 (ppm)



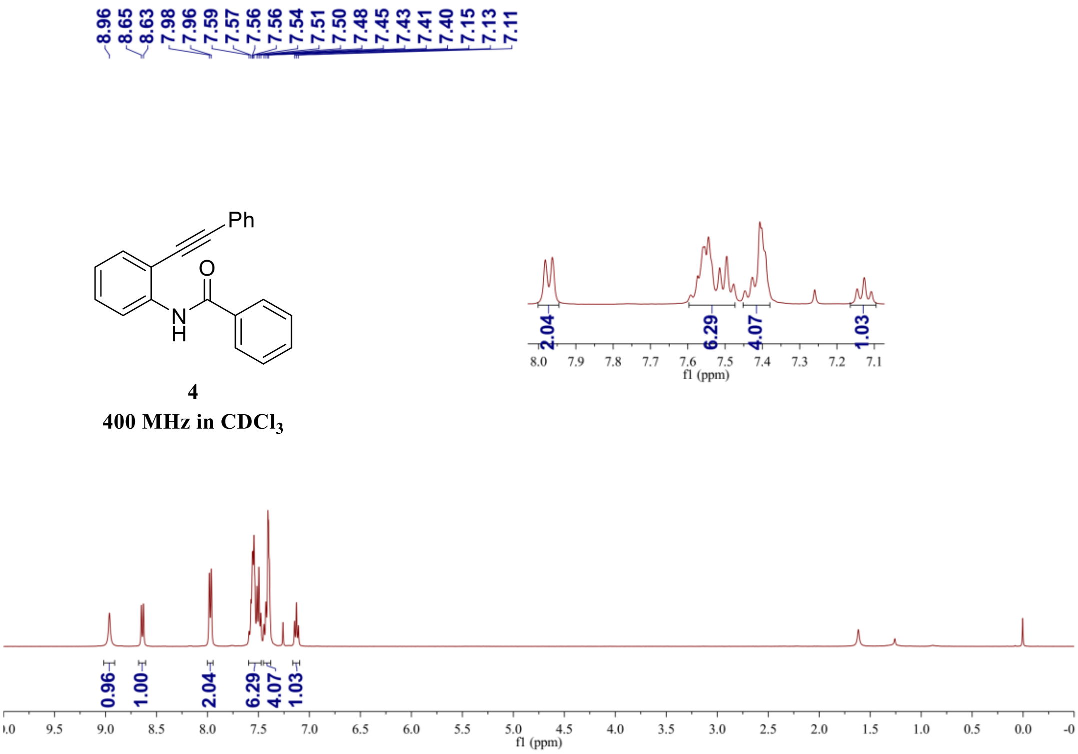
3ka

400 MHz in $CDCl_3$



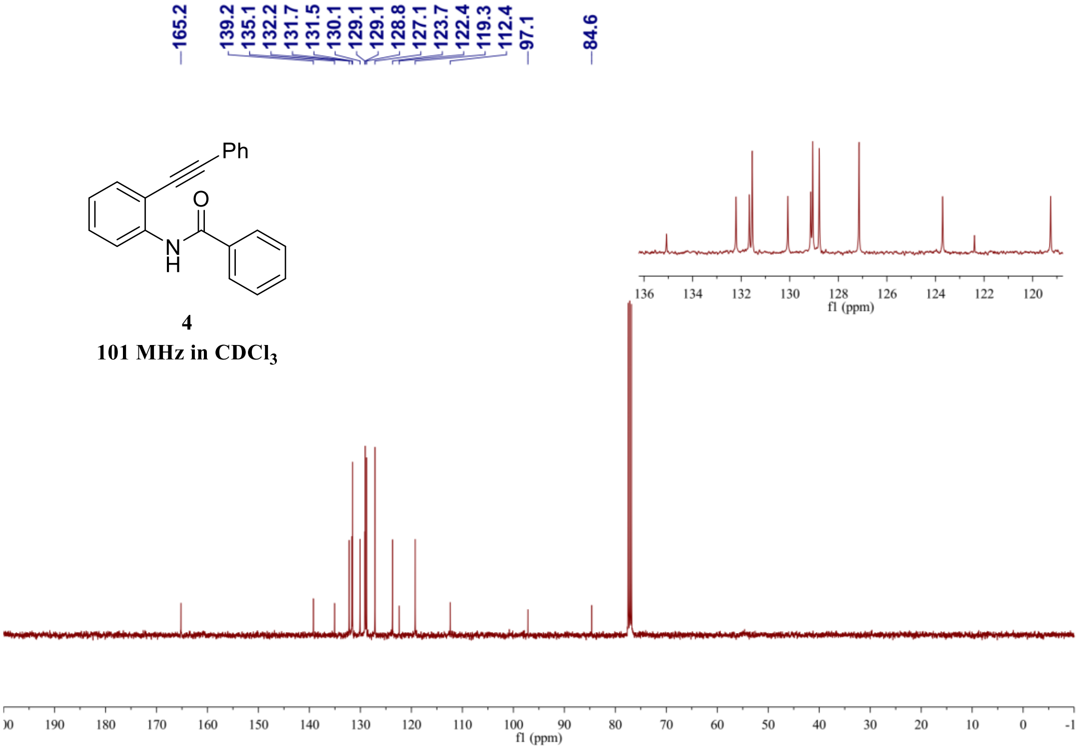
3ka

101 MHz in $CDCl_3$



4

400 MHz in $CDCl_3$



4

101 MHz in $CDCl_3$